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THE PRODUCTION OF CIS- AND TRANS-CARONIC ACIDS FROM DELTA-3-CARENE

MONTANA STATE UNIVERSITY

PREPARED FOR
FEDERAL WATER POLLUTION CONTROL
ADMINISTRATION

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Title of Report: The Production of cis- and trans-Caronic Acids from delta-3-Carene.

By James H. Jarrett

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THE PRODUCTION OF CIS- AND TRANS-CARONIC ACIDS FROM DELTA-3-CARENE

by

JAMES HUGH JARRETT

ABSTRACT

The sole known source of delta-3-carene, a bicyclic terpene, in the United States and Canada is in the by-product turpentine produced by five western Kraft pulp mills. The present potential supply of delta-3-carene is 1000 gallons per day.

Two cyclopropane ring-containing dibasic acids (cis- and trans-caronic acids) were recovered in 99% purity from the mixture of oxidation products obtained by the potassium permanganate oxidation of delta-3-carene in acetone. The yield of cis-caronic acid was 6.5% and the yield of trans-caronic acid was 0.5%.

The identification of cis- and trans-caronic acids was based on commercial analysis for carbon, hydrogen and oxygen, and on infrared and nuclear magnetic resonance spectroscopy. The spectra are included in the thesis.

Delta-3-carene, 41.4 g, was oxidized with 216.6 g potassium permanganate in 3,600 ml of acetone at a temperature of 16-18°C. The potassium permanganate reacted completely in 18 hours with a delta-3-carene conversion of 85%. Ninety-seven percent of the oxidation products were adsorbed on the surface of the manganese dioxide formed during the reaction. The unreacted delta-3-carene and 3% of the oxidation products remained in the acetone phase. The oxidation products were removed from the manganese dioxide surface with 85% efficiency by washing with hot water.

The relative solubilities of the oxidation products in water varied at different pH values. Thus, they were separated by ether extraction of a water solution with pH control. Cis-caronic acid was recovered by 1) extracting a pH = 3.0 water solution of oxidation products with ether to remove a relatively large amount of oxidation products containing a small amount of cis-caronic acid, 2) extracting the water solution again at a pH of less than one to remove a mixture of oxidation products having a high concentration of cis-caronic acid. Cis-caronic acid crystals precipitated from the pH < 1 extract and were purified by washing with chloroform.

The pH = 3.0 extract was redissolved in water, the pH adjusted to pH = 4.0 and the water solution extracted with ether. The water solution was then acidified (to pH < 1) and extracted again. More cis-caronic acid was recovered from the pH < 1 extract.

Trans-caronic acid was concentrated in the pH = 4.0 extract which also contained a mixture of crystals. It was recovered by 1) preparing the ammonium salt of the filtered extract, 2) removing excess water, 3) adding ethanol which dissolved all of the ammonium salts but ammonium trans-caronate, 4) filtering, and 5) converting ammonium trans-caronate to trans-caronic acid.

I INTRODUCTION

A. Delta-3-Carene

The first literature article on delta-3-carene appeared in 1920 (1). An article summarizing the work done on delta-3-carene and containing over 200 references was published in 1965 (2). More recent work on delta-3-carene established its structure as determined by electron diffraction (3). Further structural confirmation appeared in 1966 (4). The structure of delta-3-carene has been given as follows (4):

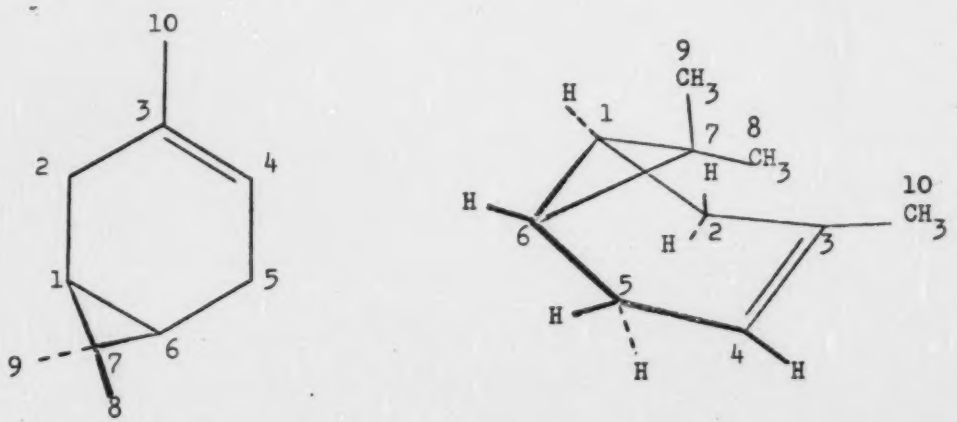

Figure 1. The Structure of Delta-3-Carene.

The sole known source of delta-3-carene in the United States and Canada is in the by-product turpentine produced by five western Kraft pulp mills (5). Only three of the five mills are presently condensing their turpentine (5). This information is summarized in Table I.

Table I. Availability of Delta-3-Carene in the United States and Canada

A. Mills producing and condensing delta-3-carene containing turpentine:

Potlatch Forests, Inc., Lewiston, Idaho
Hoerner-Waldorf Paper Products Co., Missoula, Montana
Southwest Forest Industries, Snowflake, Arizona

B. Mills producing but not condensing delta-3-carene containing turpentine:

Boise-Cascade Corporation, Wallula, Washington
Northwestern Pulp and Power, Ltd., Hinton, Alberta

The potential production of delta-3-carene from the three mills that are presently producing and condensing turpentine containing delta-3-carene is about 1000 gallons per day (6). At present, there is no known commercial use for delta-3-carene that makes its recovery and purification economically attractive.

B. Oxidation of Delta-3-Carene

The oxidation of delta-3-carene and subsequent formation and purification of dicarboxylic acids containing the cyclopropane ring has been reported before in the literature (7, 8, 9). The names and structures of these acids are shown in Figure 2. Little yield information was given in any of the oxidation articles (7, 8, 9), all of which appeared before 1930. No references have been made in the literature to either a source of any of these acids for experimental work (other than a source (17) of small samples of certain acids for analytical work) or to experimentation that could lead to their commercial development. We were not able to locate either a sample or spectra (IR, NMR) of either cis-caronic acid or dimethyl cis-caronate for analytical purposes from any outside sources (17, 18, 19).

C. Potential Utilization of Cyclopropane Ring-Containing Dicarboxylic Acids* from Delta-3-Carene

Since a convenient source of any of these acids has never been available for new product research, it is not surprising that potential industrial uses have not been reported. Dicarboxylic acids have, however, shown much use in the field of synthetic polymers such as the use of adipic acid in polyamides (e.g., nylon), and dimethyl-terephthalate from terephthalic acid in polyesters (e.g., Dacron).

* For names and structures, see Figure 2.

Figure 3 shows the formulas of conceivable polyamides using cis-caronic acid, one of the cyclopropane ring-containing dibasic acids from delta-3-carene oxidation. Figure 4 shows a potential application of cis-caronic acid in a polyester.

Dicarboxylic acids have also been used in the production of plasticizers, lubricants, coatings, elastomers and thermosetting compounds (10).

D. Incentive for Delta-3-Carene Research

The creation of a demand for delta-3-carene would lead to pollution abatement and possibly to a new industry located in Montana. Air pollution due to uncondensed turpentine bearing malodorous sulfur compounds would be eliminated in mills producing turpentine containing delta-3-carene.

II. RESEARCH OBJECTIVES

The overall goals of this research were to produce a pure cyclopropane ring containing dicarboxylic acid from delta-3-carene, and to report the yield. The research objectives were as follows:

1. Isolate and confirm the identity of *cis*- and *trans*-caronic acids.
2. Choose a delta-3-carene oxidizing agent.
3. Produce delta-3-carene oxidation product.
4. Separate *cis*- and *trans*-caronic acids from the oxidation product.
5. Report yields.

III EXPERIMENTAL

A. Esterification Using Diazomethane

It was found necessary to have available a method for the preparation, in high yield, of the methyl ester(s) of the organic acid(s) encountered in this research. The methyl ester(s) were used for infrared and nuclear magnetic resonance spectra as well as for gas-chromatography.

Since high yields were required and sample sizes were usually small (50 mg), the esterification was accomplished by the reaction of the organic acid(s) with gaseous diazomethane (11). It must be noted that diazomethane is both explosive and toxic and care must be taken in its use (11).

Method: Diazomethane (CH_2N_2) was generated by treating N-methyl-N-nitroso-p-toluenesulfonamide (Diazald*) with a 60% potassium hydroxide solution in the presence of 2-(B-ethoxy-ethoxy) ethanol (carbitol**) and anhydrous ether. The gaseous diazomethane was then bubbled into an ether solution of the acid that was to be methylated. The apparatus was set up as shown in Figure 5. It consisted of a nitrogen cylinder with a pressure regulator, two test tubes (25 x 190 mm) with side arms, a smaller sample vial (15 x 45 mm), and appropriately sized rubber stoppers.

---

* Aldrich Chemical Company, Inc., Milwaukee, Wisc.

** Van Waters & Rogers, Seattle, Wash.

The flow rate of the nitrogen sweep gas was adjusted to approximately 6 ml per minute. The gas bubbled through the first test tube which contained about 15 ml of anhydrous ether. The mixture of nitrogen and ether vapor passed from the first tube into the second tube which contained a mixture of 2 ml of carbitol, 10 ml of anhydrous ether, 2 ml of 60% potassium hydroxide solution, and 0.5 g of Diazald. The N_2 flow carried the CH_2N_2 gas from the second tube to the sample vial which contained the sample to be esterified dissolved in ether. Diazald was added to the second tube in 0.5 g increments at intervals of five minutes until the esterification was complete. Since unreacted CH_2N_2 imparted a yellow color to the solution in the sample vial, one could visually tell when the reaction was complete.

The apparatus was set up in a hood and care was taken not to breathe CH_2N_2 vapors either during the esterification or during the evaporation of the ether solvent from the sample.

B. Gas Chromatography

Gas chromatographic techniques were used both in analyzing the various mixtures of oxidation products and in preparing pure samples for spectroscopy. In all cases, samples were esterified before they were used for chromatographic work.

Analysis of Oxidation Products

Equipment: The methyl esters of the oxidation products were analyzed with a Wilkens Aerograph "Moduline" model 202 dual column gas chromatograph having a dual thermal conductivity detector. The chromatograph was used with a Sargent Model SR recorder. A 10-microliter syringe was used for injecting samples. The sample volume was from two to five microliters. The chromatograph column found to be most satisfactory was prepared here at Montana State University (see page 9). It had the following specifications:

Stationary Phase- - - - -	5% carbowax 20 M
Support - - - - - - - - -	Chromosorb T
Column - - - - - - - - -	20' x 1/4" copper
Operating Conditions - -	Column temperature 175°C
	H_2 carrier gas rate 50-70 cc/min

Analysis Techniques

Comparison of Retention Times: The principle applied in analyzing an unknown sample using gas chromatography is that a given compound has a constant retention time (the time required for the sample to pass through the chromatograph) providing the chromatograph conditions remain constant. Thus, if a known compound has a retention time of ten minutes and at the same operating conditions one of the components of an unknown sample has a retention of ten minutes, we can make the following conclusions:

1. The compound with the ten-minute retention time in the unknown sample may possibly have the same identity as that of the known compound with a retention time of ten minutes.
2. None of the other compounds in the unknown sample have the identity of the known compound with a retention time of ten minutes.

Peak Enhancement: In addition to comparing retention times, a mixture of the known sample and an unknown sample may be prepared and analyzed. When the gas chromatogram of the mixture is compared with the gas chromatogram of the original unknown sample the chromatogram of the mixture will either contain an extra peak or one of the peaks will be larger in size. If one of the peaks is made larger by the addition of a known sample, this is known as 'peak enhancement'. In the case of peak enhancement, we can conclude that:

1. The compound in the unknown sample whose peak is enhanced by the addition of a known sample may have the identity of the known sample.
2. None of the other compounds in the unknown sample whose peaks are not enhanced have the identity of the known sample.

Preparative Gas Chromatography

Preparative chromatography is a convenient means of obtaining small amounts of pure compounds for analysis such as infrared and nuclear magnetic resonance spectroscopy. It involves injecting a mixture of compounds into the gas chromatograph and then collecting

each pure compound separately at the chromatograph exit.

Equipment: The Wilkens Model 202 gas chromatograph with a thermal conductivity detector was used for preparative chromatography. A sample size of 60 to 80 microliters was used. Samples of esterified oxidation product were injected with a 100 microliter syringe. The 5% Carbowax 20 M column described on page 10 was used for preparative work.

Sample Collection: The pure compounds were collected as illustrated in Figure 6 at the chromatograph exit in pieces of 3 mm glass tubing. The tubing was inserted into a rubber septum at the chromatograph exit to prevent leakage. A loop of the tubing was immersed in liquid air to insure complete sample condensation.

Atomizing Effect: When the glass tubing at room temperature was inserted into the gas chromatograph exit which was at a temperature of about 200°C, a white vapor was observed coming out of the sample tube. The sample was apparently atomized into a fine mist at the chromatograph exit, frozen as it passed into the portion of the tube cooled by liquid air, and then carried out into the atmosphere by the chromatograph carrier gas. This atomizing effect and the resulting loss of product was eliminated by heating the end of the sample collection tube to about 100°C before it was inserted into the chromatograph exit.

Fabrication of Carbowax 20 M Column

The fabrication of the 20' x 1/4", 5% Carbowax 20 M on Chromosorb T column used for analyzing the methyl esters of the oxi-

dation products was done here at Montana State University. Carbowax 20 M (6.5 g) was dissolved in 200 ml of chloroform and the solution mixed with 123.5 g of Chromosorb T. The chloroform was then evaporated in the hood while the slurry was stirred with a magnetic stirrer.

The packing was then screened through a 40-mesh screen and poured into a 20-foot piece of copper tubing. A plug of glass wool was placed in the end of the tubing and the other end connected to a vacuum line. Approximately 90 g of packing were required to fill the tubing. Swagelok fittings were used on the ends of the column and it was coiled so that it would fit in the chromatograph oven. The column was cured in the oven for 24 hours at 200°C before using.

C. pH Measurement

A Beckman model 180 pocket pH meter was used for pH measurements. The meter was calibrated with a buffer solution having a pH value close to that of the unknown solution. Commonly used buffer solutions had pH's of 3.0, 4.0, 6.0, 7.0, 8.0, and 9.0. The reproducibility of pH measurements was found to be about $\pm$0.1 pH units.

D. Melting Point Determination

Melting points were measured with a Fisher-Johns melting point apparatus. It consisted of a 1.5 cm diameter plate that was heated electrically. The temperature was measured with a thermometer that was mounted in the plate. A few crystals of the sample were

placed between two cover glasses which were put on the plate. The heating rate of the plate was controlled with a dial that had scale readings from zero to one hundred.

The dial was set at fifty to get an approximate idea of the melting point. Another determination was then made, turning the dial to thirty at 10°C below the melting point. This gave a slower heating rate near the melting point of the crystal.

Using the above procedure, the melting point of adipic acid (151.4°C) was found experimentally to be 151-152°C.

E. Ether Extraction

The use of ether extraction to remove organic compounds dissolved in water is a common technique. It was applied to remove dissolved delta-3-carene oxidation products from water solutions. Both manual and continuous ether extractions were used.

Manual Extraction

A separatory funnel was used for manual extractions. The volume of ether used in a single extraction was equal to half the volume of the water phase. Thus, in extracting 100 ml of water solution four times with ether, a total volume of 200 ml of ether was required.

Continuous Extraction

The apparatus used for continuous extraction is illustrated in Figure 8. Ether was boiled in the stillpot, the vapors passed up into the cold water condenser, and liquid ether dripped into the

funnel. The funnel carried the liquid ether to the bottom of the water phase where it then passed through the water phase and up to the ether layer. The use of a magnetic stirrer in the water phase increased water-ether contact.

To complete the cycle, the solution of the ether plus the organic material extracted from the water phase ran down the side arm and back to the stillpot where the ether was evaporated to continue the cycle. The high boiling material extracted from the water phase concentrated in the stillpot. The continuous extraction system was usually run 24 hours for each water solution.

Removal of Water from Ether Extracts

During the mixing of ether and water, some water dissolved in the ether phase. At equilibrium the solubility of water in ether at 20°C is 7.5 g per 100 ml of ether (16). When quantitative information on the amount of organic material in an ether extract was desired, the water in the extract had to be removed.

Use of Anhydrous Magnesium Sulfate as a Drying Agent: Since the organic material in the ether extracts encountered in this research could be expected to include materials volatile at room temperature, a chemical drying agent -- anhydrous magnesium sulfate -- was used in the following procedure for drying 100 ml of extract:

1. Ten grams of anhydrous magnesium sulfate were added and the mixture allowed to stand 20 minutes with occasional stirring.

2. The solid material was removed by vacuum filtration.

3. Steps 1 and 2 were repeated two times.

Extraction Efficiency

The efficiencies of both manual and continuous extractions were investigated on the product from the potassium permanganate oxidations of delta-3-carene in acetone (Section III-L). The product was left in the hood until it attained a nearly constant weight. At a weight of 3.68 g, the oxidation product had lost 0.05 g in the previous 14.5 hours.

A solution was made of 3.51 g of oxidation product and 100 ml of water. The solution was acidified to a pH = 1.4 by the addition of 4 ml of concentrated hydrochloric acid, and extracted manually four times with a total volume of 200 ml of ether. Upon drying with magnesium sulfate (Section III-E) and evaporating the ether, 2.26 g (64.4%) of oxidation product were recovered.

The raffinate water solution was diluted to 500 ml with water and 5 ml of concentrated hydrochloric acid was added to adjust the pH from 2.3 to 1.8. The water solution was next extracted continuously with ether for 24 hours. Upon drying the extract with magnesium sulfate (page 12) and evaporating the ether, 0.95 or 76% of the remaining oxidation product was removed by continuous extraction. The residual concentration of oxidation product in the water after con-

tinuous extraction was 0.13 g or 0.26 g/liter. A total of 3.21 g or 91.6% of the oxidation products was removed from the water solution.

F. Spectroscopy

Both infrared and nuclear magnetic resonance spectroscopy were used in the analysis work involved with this project.

Infrared Spectroscopy

The infrared spectra were run on a Beckman IR-4 spectrophotometer in the Chemistry Department of Montana State University. The majority of the spectra were taken with the sample dissolved in carbon tetrachloride. The solvent peaks were compensated out by placing a carbon tetrachloride filled wedge cell in the reference beam. Typical operating conditions for the Beckman IR-4 unit were as follows:

Sample	Ester
path	0.5 mm
solvent	CCl_4
Reference	Wedge Cell
solvent	CCl_4
Scale	0.09 Kaysers per in.
Period	2
Slit sched.	0.11 at 2828 Kaysers
Ordinate scale	DB
Gain	5.0 x 10

A blank spectrum is shown in Figure 26. This shows a typical compensation of the carbon tetrachloride peak in the solvent by the carbon tetrachloride placed in the reference beam.

Nuclear Magnetic Resonance Spectroscopy

The NMR spectrum of a compound is useful in giving an indication of the relative number and molecular environment of the protons in the molecule. The relative number of protons is directly related to the peak area. The areas are measured on the NMR spectrophotometer by using its integrating circuit. Thus, the NMR spectrum of a compound consists of the peaks at various locations representing the proton environment, and of the horizontal "stair-step" line. The vertical distance between the horizontal lines is an indication of the relative peak area.

The NMR spectra were run on a Varian model A-60 spectrophotometer in the Chemistry Department of Montana State University. The procedure outlined in the A-60 operations manual was used for tuning the NMR unit. A typical set of operating conditions was as follows:

Solvent - - - - - - - - $CDCl_3$
Temperature - - - - - - - ambient
Filter Bandwidth - - - 4 cps
R. F. Field - - - - - - - 0.3 mG
Sweep Time - - - - - - - 500 cps
Sweep Width - - - - - - - 500 cps

Sweep Offset - - - - - 0 cps
Spectrum Amplitude - - 4 to 16
Integral Amplitude - - 80

G. Commercial Analysis

Samples of various pure products were sent to the Huffman Laboratories, P. O. Box 350, Wheatridge, Colorado for analysis. Samples were analyzed for percent carbon, hydrogen, oxygen, and molecular weight. The ebullioscopic or boiling point elevation method was used for measurement of molecular weight.

The experimental error for the analysis was estimated by Dr. E.W.D. Huffman as follows (12):

carbon - - - - - - - - - - - within ± 0.3% absolute
hydrogen - - - - - - - - - - within ± 0.3% absolute
oxygen - - - - - - - - - - within ± 0.5% absolute
molecular weight - usually within ± 10% relative

H. Trans-Caronic Acid from Ethyl Trans-Chrysanthemate

A sample of trans-caronic acid was prepared from ethyl trans-chrysanthemate for comparison with trans-caronic acid from delta-3-carene (Section III-M). The trans-caronic acid was esterified to dimethyl trans-caronate for gas chromatography, and infrared and nuclear magnetic resonance spectroscopy. The acid was also used for melting point determinations.

Trans-caronic acid was prepared from ethyl chrysanthemate by the following method:

ethyl chrysanthemate chrysanthemic acid trans-caronic acid

The optimum hydrolysis conditions found were as follows:

1.0 g NaOH
2.0 g ester
10 ml ethanol
20 ml water

→ reflux 3.3 hours → recover acid and ester → 0.23 g ester, 1.31 g acid

The ester was recovered from the basic hydrolysis mixture by ether extraction after the ethanol was removed by evaporation. The acid was then recovered by ether extraction of the acidified (pH <1) hydrolysis mixture.

A periodate-permanganate oxidation was used to oxidize chrysanthemic acid. Mixtures A and B were combined and allowed to stand for 24 hours.

chrysanthemic acid - - - - - - 1.68 g
potassium carbonate, K_2CO_3 - 4.14 g
water - - - - - - - - - - - - 1000 ml

Mixture A

sodium periodate, $NaIO_4$	1.68 g	
potassium permanganate, $KMnO_4$	0.32 g	Mixture B
water	1000 ml	

At the end of 24 hours, 200 ml of 10% H_2SO_4 were added, and sodium bisulfite was added to react with the manganese dioxide present to form manganous sulfate. The volume of the solution was reduced to 600 ml by air evaporation. The pH of the resulting solution was 1.4. It was next extracted continuously with ether* for 24 hours. Upon drying with anhydrous magnesium sulfate (Section III-E) and evaporating the ether, 2.11 g of oxidation product were recovered.

Trans-caronic acid was isolated from the oxidation products by the following procedure:

1. The ammonium salt of the product mixture was prepared by adding an excess of concentrated ammonium hydroxide.
2. The excess water and ammonia were removed by evaporation.
3. One part of 100% ethanol was added to one part of ammonium salt. All salts but the ammonium trans-caronate dissolved, so the mixture was filtered to recover the ammonium trans-caronate.
4. The ammonium trans-caronate was re-crystallized from hot water.

* See Section III-E for description of continuous extraction.

5. The ammonium trans-caronate was converted to caronic acid by the addition of concentrated hydrochloric acid to a water solution of the ammonium salt, and the caronic acid removed from the acidic water solution by ether extraction.

The yield of pure trans-caronic acid was about 0.2 g or 12.7%. The above method for trans-caronic acid recovery was described in the literature (7).

I. Dimethyl Cis- and Trans-Caronate by Preparative Chromatography

Analytical samples of dimethyl cis- and trans-caronate were prepared here at Montana State University. As discussed before, trans-caronic acid was also obtained from ethyl chrysanthemate (Section III-H).

The oxidation product resulting from the $KMnO_4$ oxidation of delta-3-carene in acetone was esterified to form the feedstock for the preparative chromatography. Since the purpose of the preparative chromatography was to collect dimethyl cis- and trans-caronate for identification purposes, it was not known which peaks in the oxidation product were dimethyl cis- and trans-caronate. Therefore, pure samples of the methyl esters of all the major oxidation products were collected.

J. Catalytic Liquid-Phase Air Oxidation of Delta-3-Carene

No report has been made in the literature of the catalytic liquid-phase air oxidation of delta-3-carene. The experimental work done in this area was patterned after a process that was successful in obtaining 70-80% yields of terephthalic acid from para-xylene (14). In the para-xylene system a typical set of conditions for a batch reaction was as follows:

para-xylene feed	75 g
acetic acid solvent	150 g
cobalt acetate tetrahydrate	1.0 g
ammonium bromide	0.75 g
amount of air bubbled into reactor	10% over theoretical
temperature	195-205°C
pressure	400 psi
reaction time	2 hours
yield (mole % terephthalic acid)	79%

Four other bromine-containing materials besides ammonium bromide were also tried; these were benzyl bromide, bromine, potassium bromate, and acetylene tetrabromide. Two other metal compounds, manganese acetate tetrahydrate and ammonium molybdate, were tested in addition to cobalt acetate tetrahydrate.

Laboratory System

In applying the above work to the oxidation of delta-3-carene, the following set of conditions was used:

delta-3-carene feed (99% purity)	30.4 g
acetic acid solvent	47.5 g
cobalt acetate tetrahydrate	0.3 g

potassium bromate	0.3 g
amt. of air bubbled into reactor	4.5 ft^3
temperature	70-110°C
pressure	1 atm
reaction time	2 hrs

The amount of air used, 4.5 ft^3 at a pressure of 622 mm Hg and a temperature of 25°C, corresponds to 4.0 mols O_2 per mol of delta-3-carene.

The reaction system was set up as shown in Figure 8. The flow of air into and out of the system was measured and a demister made of glass wool prevented the air flow from sweeping delta-3-carene and acetic acid vapors from the system.

Bromine-Containing Materials

Both bromine and potassium bromate were investigated as representative bromine-containing materials. Potassium bromate was considered preferable since bromine reacted rapidly with the delta-3-carene and since 30% of the delta-3-carene was isomerized when it was refluxed for two hours at 110°C with acetic acid and bromine. Only a small amount (two percent) of isomerization was observed when delta-3-carene was refluxed under similar conditions with acetic acid and potassium bromate. It was also found that two percent of the delta-3-carene was isomerized when it was refluxed two hours with acetic acid, potassium bromate, and cobalt acetate tetrahydrate.

Reaction Product

Under conditions used the conversion of delta-3-carene was approximately 26%. Gas chromatographic analysis of the methyl ester of the oxidation product showed that it contained five different components, all in nearly like amounts, none of which was caronic acid.

K. Dichromate Oxidation of Delta-3-Carene

Delta-3-carene was oxidized with Beckman's chromic acid mixture (15) in an attempt to duplicate the work of Gibson and Simonsen (9) reported in 1929. They reported the recovery of 10 g of trans-caronic acid per 189 g of delta-3-carene, or a yield of 4.5 mol percent.

Laboratory System

The following reaction mixture was placed in a 1000 ml Erlenmeyer flask at 25°C and stirred with a magnetic stirrer until all of the dichromate solution reacted (five days).

Reaction Mixture

120 g $K_2Cr_2O_7$
93.2 ml 66°B_e H_2SO_4 } 640 ml Beckman Solution
540 ml H_2O

27.6 g delta-3-carene (99% purity)

The oxidation products and unreacted delta-3-carene were removed from the acidic water solution (pH less than 2.0) by extracting it continuously with ether for 24 hours. Continuous extraction is

discussed in Section III-E, and the apparatus used for continuous extraction is illustrated in Figure 7.

Upon drying the ether extract with anhydrous magnesium sulfate and removing the ether by evaporation, a total of 11.1 g of products was recovered. The products were dissolved in 150 ml water and the solution made basic by the addition of 7.5 g NaOH. The basic water solution was manually extracted three times with a total volume of 225 ml of ether. After drying the extract with magnesium sulfate and removing the ether by evaporation, a total of 1.4 g of neutral material was recovered.

After extraction of the basic water solution of the oxidation products, 24 ml of concentrated HCl were added to the solution. A pH = 1.6 solution resulted. This solution was manually extracted with a total volume of 225 ml ether. The extract was dried with anhydrous magnesium sulfate and the ether removed by evaporation to yield 2.6 g of rust-colored product. After standing about 24 hours, crystals formed in the product mixture. Chloroform (10 ml) was added to the mixture and 0.6 g of crystals were removed by vacuum filtration.

Reaction Product

The above procedure used to recover the 0.6 g of crystal was essentially the same as that used by Gibson and Simonsen (9) to recover trans-caronic acid. The infrared spectrum of the methyl ester of the crystal (Figure 11) showed a strong absorption at 1780 cm^{-1}

as well as a strong absorption at 1740 cm^{-1}. This indicated that the ester was not dimethyl trans-caronate but in all probability was a lactone. Gas chromatographic analysis also showed that the crystal was not trans-caronic acid.

L. Potassium Permanganate Oxidation of Delta-3-Carene in Acetone

The potassium permanganate oxidation of delta-3-carene in acetone was reported in 1923 by Simonsen and Rao (7). The following reaction system was used:

delta-3-carene - - - - - - -	40 g
potassium permanganate - -	96 g
acetone - - - - - - - - - - -	400 ml
temperature - - - - - - - -	0°C

After all of the potassium permanganate had reacted, the MnO_2 was removed by filtration and washed with hot water to remove the delta-3-carene oxidation products. The oxidation products were removed from the water solution by ether extraction. Next, the ethyl esters were formed and separated into five fractions by vacuum distillation. Upon ester hydrolysis, cis-caronic acid precipitated in one of the fractions and was recovered in an unreported yield.

An approximate yield of 0.5% of trans-caronic acid was reported. The ammonium salt of one of the fractions was prepared, and after removing excess water by evaporation, ethanol was added to the mixture of ammonium salts. All of the salts dissolved except the ammonium-trans-caronate, which was recovered by filtration.

Oxidation Reaction

In the Montana State University research the reaction mixture was placed in a 4000 ml Erlenmeyer flask and stirred. The flask was kept in a cold water bath as shown in Figure 9. The following system was used:

delta-3-carene feed (99% purity)	41.4 g
potassium permanganate	216.6 g
acetone	3,600 ml
water bath temperature	14.6°C
temp. range of reaction mixture	15-18°C
reaction time	18 hours

The solubility of potassium permanganate in acetone was found to be:

1.96 g/100 ml at 24°C

1.84 g/100 ml at 15.5°C

The rate of oxidation of acetone by potassium permanganate at 16°C is very slow. A saturated solution of potassium permanganate and acetone was prepared and 100 ml of the solution were placed in an Erlenmeyer flask and kept at 16°C for 18 hours. The solution was then filtered, removing 0.18 g of MnO_2. Thus, in the oxidation of delta-3-carene in acetone, about 11.8 g out of 216.6 g of potassium permanganate were used in oxidizing acetone.

Recovery of Oxidation Products

Most of the oxidation products were found to be adsorbed on the manganese dioxide formed during the reaction. Of the 44.0 g of

oxidation product recovered, only 1.3 g were in the acetone phase.

Two methods were used to recover the oxidation products from the solid manganese dioxide. The first method was to make a slurry of one part manganese dioxide and five parts water, and to then convert the manganese dioxide to manganous sulfate by the action of either sodium bisulfite or gaseous sulfur dioxide. The result was a water solution of the oxidation products and manganous sulfate that can be extracted with ether, and the ether evaporated to yield the recovered oxidation products.

The second method was to wash the manganese dioxide with hot water. A slurry of one part manganese dioxide and three parts water was heated and then filtered. This process was repeated until the filtrate was water-white. A total of 30 parts of water were used to wash one part of manganese dioxide.

Efficiency of Water Wash: Using the previously mentioned set of conditions for the oxidation reaction, the theoretical amount of manganese dioxide formed was 120 g. After the manganese dioxide was water washed, it was dried to a constant weight of 127 g. This implied that about seven grams of oxidation products were left on the manganese dioxide.

Unreacted Delta-3-Carene

Of the 41.4 g of initial delta-3-carene in the oxidation system, 6.0 g were not oxidized. The unreacted delta-3-carene re-

mained in the acetone phase along with 1.3 g of oxidation products. There was an 85.4% conversion of the delta-3-carene charge to oxidation products.

M. Separation of the Oxidation Products Resulting from the Potassium Permanganate Oxidation of Delta-3-Carene in Acetone

The method previously used to separate the mixture of oxidation products from the potassium permanganate oxidation of delta-3-carene in acetone was to vacuum distill the ethyl esters of the oxidation products (7). After separating the mixture of esters into different boiling point fractions the esters were hydrolyzed back to the acids and certain acids precipitated out of the different fractions.

The technique that was used in this research has never before been reported in the literature for the separation of delta-3-carene oxidation products. It involved the ether extraction of a water solution of the oxidation products with pH control. At various pH levels the relative solubilities of the different oxidation products in the water phase changed enough to give a separation of oxidation products when the water phase was extracted at a given pH, the pH readjusted to a new level, and the solution extracted again.

Recovery of Cis-Caronic Acid

Cis-caronic acid was recovered from the mixture of oxidation products (Figure 13) resulting from the oxidation of 35.4 g of delta-3-carene by 217 g of potassium permanganate in 3,600 ml of acetone at 16°C. The oxidation products were recovered from the manganese dioxide surface by washing with hot water, as explained in Section III-L.

The volume of the water solution of the oxidation products was reduced to 200 ml. The pH of the concentrated water solution was adjusted to 3.0 by adding 70 ml of concentrated hydrochloric acid, and the solution extracted manually four times with a total volume of 400 ml of ether. The result, upon drying with anhydrous magnesium sulfate and removing the ether by evaporation, was a mixture of 28.0 g of oxidation products (Figure 14) that contained a much smaller relative amount of cis-caronic acid than original mixture of oxidation products. This extract was saved for recycle.

The pH of the water solution was next adjusted to less than one, and the solution extracted manually as before. The mixture of 11.5 g of oxidation products from this extraction (Figure 15) contained a high enough relative amount of cis-caronic acid for it to precipitate out of the mixture.

The cis-caronic acid crystals were removed from the mixture of oxidation products by vacuum filtration of a mixture of the oxi-

dation products and an equal volume of chloroform. In this manner, 1.8 g of white cis-caronic acid crystals were recovered.

The solvent was removed from the filtrate by evaporation and a few more crystals formed in the mixture in a period of ten days. Using the same recovery procedure another 0.30 g of cis-caronic acid was obtained. The gas chromatogram of the methyl ester of the mixture of oxidation products after removal of the caronic acid precipitate is shown in Figure 15.

The 28.0 g of recycle extract from the pH = 3.0 water solution were dissolved in 100 ml of water, the pH adjusted to 4.0 by adding 3.0 g of potassium hydroxide, and the solution extracted manually four times with a total volume of 200 ml of ether. Upon water removal (Section III-E) and ether evaporation, 19.8 g of oxidation products remained (Figure 16). The water solution was adjusted to a pH of less than one and manually extracted as before. After drying and removing the ether by evaporation, 7.4 g of oxidation product (Figure 17) were left, including some crystals of cis-caronic acid. The crystalline cis-caronic acid was recovered as before in an amount of 0.6 g. The methyl ester of the extract after caronic acid removal is shown in Figure 17. The overall yield of cis-caronic acid was 2.7 g from 35.4 g of delta-3-carene, or 6.5 mol percent.

In order to obtain representative weights of the various extracts after ether evaporation the original ether extracts were dried with anhydrous magnesium sulfate to remove water (Section III-E). The

ether was evaporated in the hood and the extracts weighed after about 15 hours when no smell of ether could be detected.

Recovery of Trans-Caronic Acid

The small amount of trans-caronic acid formed in the potassium permanganate oxidation of delta-3-carene in acetone at 16°C was found to be concentrated in the 19.8 g of pH = 4.0 extract (Figure 16) mentioned in the previous section on the recovery of cis-caronic acid.

The method used for the recovery of trans-caronic acid from a mixture of delta-3-carene oxidation products was first reported in 1923 (7). A similar procedure was used in this research. The crystals in the pH = 4.0 extract were first removed (see discussion in next paragraph), and the ammonium salts of the remaining oxidation products were prepared by adding an excess of concentrated ammonium hydroxide to a water solution of the oxidation products (one part oxidation products plus one part water). The water was removed by evaporation, with the last traces being removed in a vacuum oven. Ethanol was then added to the dry mixture of ammonium salts and all dissolved but the ammonium trans-caronate. The ammonium trans-caronate was removed by filtration, hydrolized back to the acid, and removed from the hydrolysis solution by ether extraction. A yield of about 0.5% was obtained.

Crystal from pH = 4.0 Extract

A total of 3.4 g of a crystalline material, melting point = 114-116°C, was removed from the 19.8 g of pH = 4.0 extract. The

method of crystal separation and purification used for cis-caronic acid was repeated on the pH = 4.0 extract.

Upon gas chromatographic analysis of the methyl ester of the crystal it apparently was composed of a mixture of two compounds (Figure 16). The possibility of incomplete esterification was eliminated by re-esterifying the sample and noting no change in relative peak sizes on the chromatograph.

The possibility of a reaction in the chromatograph causing the second peak was investigated by obtaining pure samples of both products by preparative chromatography and re-injecting each back into the chromatograph. This analysis of the pure products showed only a single peak for each, thus eliminating the possibility of reaction in the chromatograph. It was concluded that the white crystalline material was either a mixture of two different materials or a single material whose methyl ester decomposed into two different compounds in the gas chromatograph.

The compound having the lower retention time in the gas chromatograph was identified as dimethyl cis-homocaronate. The second compound was shown to be the methyl ester of a hydroxy carboxylic acid.*

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* For a discussion of the identification work, see Section IV.

N. Batch Process for the Production of Cis-Caronic Acid Via Potassium Permanganate Oxidation of Delta-3-Carene in Acetone

A laboratory scale batch process has been developed for the production of cis-caronic acid in 6.5 percent yield. The flow sheet is given in Figure 18. The process involves the potassium permanganate oxidation of delta-3-carene in acetone (Section III-L). The oxidation products are removed from the surface of the manganese dioxide by washing with hot water (also Section III-L). The method used for product separation is explained in Section III-M.

IV DISCUSSION OF RESULTS

A. Identification of Products

The laboratory techniques used for compound identification were discussed in Section III. Samples of trans-caronic acid, cis-homocaronic acid and trans-homocaronic acid were obtained from Dr. Masanao Matsui, University of Tokyo, Tokyo, Japan (17). The infrared spectra of methyl esters of these compounds are shown in Figures 19, 22, and 24. Both E. J. Corey (18) and E. M. Eyring (19) were contacted but were unable to furnish either samples or spectra of any desired compounds.

Cis-Caronic Acid

The production of 99% purity cis-caronic acid from delta-3-carene in 6.5% yield was discussed in Sections III-M and III-N. The melting point was 184-6°C, as determined with the Fisher-Johns melting point apparatus (Section III-D). The melting point reported in the literature is 176-8°C (19).

Dimethyl cis-caronate formed from cis-caronic acid by reaction with diazomethane (Section III-A) was shown by gas chromatography to be 99% pure. The infrared spectrum of pure dimethyl cis-caronate is shown in Figure 20. The nuclear magnetic resonance spectrum is shown in Figure 27. It indicates the proper hydrogen ratios; 6-H methyl ester, 2-H cyclopropane ring, and 6-H gem dimethyl. The NMR spectrum of dimethyl cis-caronate is compared with that of dimethyl trans-caronate in Section IV-C.

Both cis-caronic acid and dimethyl cis-caronate were analyzed commercially (Section III-G) with the following results:

Compound	Analysis	Expected Value, %	Value Found, %	Mol. Weight Method
Cis-Caronic Acid	Carbon	52.3	52.7 (Res. 0.8)	ebullio-
	Hydrogen	6.3	6.3	scopic in
	Oxygen	40.5	40.1	acetone
	Mol. Wt.	158	166	
Dimethyl Cis-Caronate	Carbon	58.1	58.2	ebullio-
	Hydrogen	7.5	7.6	scopic in
	Oxygen	34.4	34.7	acetone
	Mol. Wt.	186	143	

The carbon, hydrogen, oxygen values were within experimental error (Section III-G) present in the analysis. The ebullioscopic or boiling point elevation method was used for molecular weight determinations. Acetone was used as the solvent. The molecular weight for the acid was within experimental error. The molecular weight reported for the ester was low. The approximate range for experimental error was 167-205. The low value, 143, at least indicated that the molecular formula should be $C_9H_{14}O_4$ rather than C_4 or $_5H_7O_2$ or $C_{18}H_{28}O_8$.

Trans-Caronic Acid

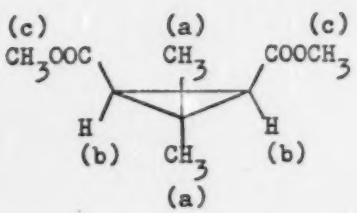
This acid was produced from delta-3-carene in a yield of about 0.5% (Section III-M). The melting point of the pure acid was 212-14°C. The literature value was 212-13°C (7).

The trans-caronic acid from this research and the trans-caronic acid from Dr. M. Matsui, University of Tokyo, were compared. The gas chromatographic retention times of the methyl esters were identical. The infrared spectra of the methyl esters (Figures 19 and 20) are essentially the same.

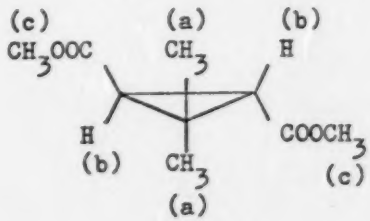
The nuclear magnetic resonance spectrum (Figure 27) shows the proper hydrogen ratios; 6-H methyl ester, 2-H cyclopropane ring, 6-H gem-dimethyl.

Comparison of NMR Spectra of Dimethyl Cis- and Trans-Caronate

The NMR spectra are shown in Figure 27. The spectra are summarized as follows:



Dimethyl Cis-Caronate



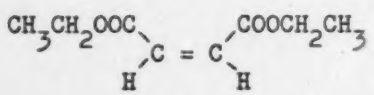
Dimethyl Trans-Caronate

Proton Location	Peak Position, δ ppm Cis-	Trans-	Proton Ratio
(a) gem-dimethyl	1.2 & 1.4	1.2	6
(b) cyclopropane Ring	1.9	2.3	2
(c) methyl ester	3.6	3.7	6

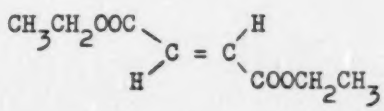
The proton ratios are correct. The splitting of the gem-dimethyl peak, δ = 1.2 and 1.4, of dimethyl cis-caronate is expected since the hydrogens of the two methyl groups are not in the same molecular environment. The gem-dimethyl groups of dimethyl trans-caronate are in identical environments, and the NMR peak, δ = 1.2, is not split.

The peak for the cyclopropane ring hydrogens in dimethyl cis-caronate is at δ = 1.9 ppm. Here the hydrogens are cis on the cyclopropane ring. In dimethyl trans-caronate the hydrogens are trans on the cyclopropane ring. The NMR peak is shifted to a lower field location, δ = 2.3 ppm. The peak locations indicate that the ring protons in dimethyl cis-caronate are more highly shielded or have a higher electron density around the protons than do the ring protons in dimethyl trans-caronate (20).

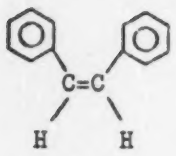
An analogous shift exists when the protons are cis and trans to one another on a carbon carbon double bond. The peak shifts are shown below (21):



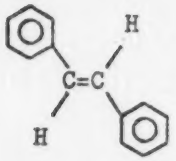
Diethyl Maleate



Diethyl Fumarate



Cis-Stilbene



Trans-Stilbene

Compound	Proton Location	Peak Position, δ ppm.	Shift, δ ppm (trans - cis)
Dimethyl Trans-Caronate I	trans on ring	2.3	0.4
Dimethyl Cis-Caronate	cis on ring	1.9	
Diethyl Fumarate	trans on C=C	6.8	0.5
Diethyl Maleate	cis on C=C	6.3	
Trans-Stilbene	trans on C=C	7.1	0.5
Cis-Stilbene	cis on C=C	6.6	

Cis-Homocaronic Acid

Cis-homocaronic acid was present in the crystal recovered from the pH = 4.0 extract (Section III-M). The gas chromatogram of the methyl ester of the precipitate is shown in Figure 16. The first peak is dimethyl cis-homocaronate. It was separated by preparative

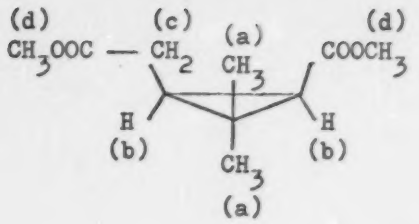
chromatography (Section III-B). The infrared spectrum of our dimethyl cis-homocaronate is shown in Figure 22. This spectrum compares well with the infrared spectrum (Figure 23) of dimethyl cis-homocaronate prepared from the cis-homocaronic acid sample obtained from Dr. M. Matsui, University of Tokyo.

The gas chromatographic retention times of the University of Tokyo and Montana State University dimethyl cis-caronates are identical.

The commercial analysis (Section III-G) of the Montana State University dimethyl cis-homocaronate shows good agreement with expected values, as shown below:

Compound	Analysis	Expected Value, %	Value Found, %	Mol. Weight Method
Dimethyl Cis-Homocaronate	Carbon	60.0	60.4	ebullio-
	Hydrogen	8.0	8.1	scopic,
$C_{10}H_{16}O_4$	Oxygen	32.0	32.0	$CHCl_3$
	Mol. Wt.	200	246	solvent

The nuclear magnetic resonance spectrum shows the following hydrogen ratios and peak positions:



Dimethyl Cis-Homocaronate

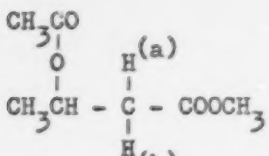
Proton Location	Peak Position, δ ppm	Proton Ratio
(a) gem-dimethyl	1.2	6
(b) cyclopropane ring	1.5-1.6	2
(c) methylene group	2.75, 2.9	2
(d) methyl ester	3.65, 3.7	6

The proton ratios fit the structure of dimethyl cis-homocaronate. One might expect the gem-dimethyl peak to be split as it is in dimethyl cis-caronate, but an examination of a model of the molecule shows that the gem-dimethyl groups are in similar environments relative to the methyl carboxylate groups. This accounts for the single peak.

The protons on the cyclopropane ring show a number of small peaks at δ = 1.5-1.6 ppm. This location is close to the peak loca-

tion (δ = 1.9) of the protons on the ring in dimethyl cis-caronate (Figure 26).

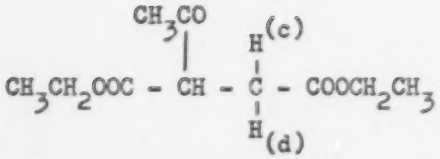
The methylene peaks may be compared to the methylene peaks in the following two compounds (21):



(a) δ = 2.5 or 2.7 ppm

(b) δ = 2.5 or 2.7 ppm

β - Acetoxy Methyl Butyrate



(c) δ = 2.86 ppm

(d) δ = 2.89 ppm

Diethyl Acetylsuccinate

In each of the compounds the two methylene peaks are in slightly different locations. The peak positions are similar to those of dimethyl cis-homocaronate.

The small difference in location of the two peaks for the protons in the methyl ester peaks is expected because the two groups are in slightly different environments. The peak location is similar

to the methyl ester peaks in dimethyl cis- and trans-caronate (Figure 27).

Hydroxy Carboxylic Acid

The infrared spectrum (Figure 24) of the methyl ester of the second compound in the crystal removed from the pH = 4.0 extract (Section III-M) indicates that it contains a hydroxy group. The IR spectrum also indicates that there is no intramolecular hydrogen bonding (22), and that in carbon tetrachloride solution in a cell of 0.5 mm path length there is no intermolecular hydrogen bonding.

The commercial analysis for percent carbon, hydrogen, and oxygen is shown below:

Commercial Analysis	Value Found, %	Molecular Formula to Fit Commercial Analysis	Mol. Wt.	Comments
Carbon	58.6	$C_{7.1}H_{11.9}O_{3.0}$	144	a good possibility
Hydrogen	8.2	$C_{9.4}H_{15.7}O_{4.0}$	188	out
Oxygen	33.2	$C_{12.0}H_{20.0}O_{5.0}$	244	nearly eliminated by NMR spectrum
Mol. Wt.	208*			

*Molecular Weight Method: Ebullioscopic, $CHCl_3$ solvent.

The NMR spectrum is difficult to analyze since the gem-dimethyl peaks, δ = 1.2, 1.4, are not the same size or shape.

A positive identification of the compound was not made.

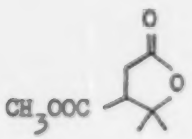
Solid Product from Dichromate Oxidation

The infrared spectrum (Figure 11) of the methyl ester of this product indicates that it has a lactone type structure. This is indicated by the strong absorption at 1780 cm^{-1}. The strong absorption at 1740 cm^{-1} indicates that the molecule also contains an ester group (22).

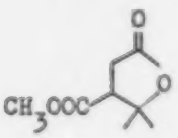
The nuclear magnetic resonance spectrum of the methyl ester showed the following:

Proton Location	Peak Position, δ ppm	Proton Ratio
gem-dimethyl	1.25, 1.6	6
methyl ester	3.7	3
other protons	2.6 - 3.4	3

The ester has been tentatively identified as methyl-terebate,



and the original solid product tentatively identified as terebic acid,



B. Choice of Oxidizing Agent

Three different oxidizing agents were investigated; potassium dichromate, air, and potassium permanganate in acetone. The experimental procedures and results for each system were covered in Sections III-J, -K, and -L.

Potassium permanganate in acetone was chosen because the oxidation product contained cis- and trans-caronic acids and cis-homocaronic acid. The system also has the advantage that the unreacted delta-3-carene remains in the acetone while most of the oxidation products (95% by weight) are adsorbed on the manganese dioxide formed in the reaction.

The products from the dichromate oxidation contained only trace amounts of the caronic and homocaronic acids. The crystalline product recovered from the mixture of oxidation products had a lactone type structure (Section IV-A).

At the conditions used for air oxidation there was a low conversion (20%) of delta-3-carene and there were no caronic or homocaronic acids in the mixture of oxidation products. Air oxidation should not be eliminated from future experimental considerations since more strenuous conditions that could lead to higher conversions were not attempted.

C. Potassium Permanganate Oxidation of Delta-3-Carene in Acetone

The important experimental results and techniques were presented in Section III-L. Potassium permanganate in acetone was chosen as an oxidizing agent because the caronic and homo-caronic acids were present in the oxidation product (Section IV-B).

Oxidation Reaction

The oxidation reaction was run at a single set of conditions. Because of time limitations no attempt was made to investigate the effects of the different reaction variables (temperature and concentrations) on the amount and distribution of oxidation products. The important reaction variables are listed and discussed.

Temperature: The temperature affects the reaction rate and the concentration of potassium permanganate. The concentration of potassium permanganate increases as temperature is increased.

Moles $KMnO_4$/Mol Delta-3-Carene: The overall amount of oxidizing agent used affects the product distribution and conversion of delta-3-carene. In this research the ratio was about 6.5 mols $KMnO_4$/mol of delta-3-carene.

Amount of Acetone Solvent/Mol Delta-3-Carene: The amount of solvent used affects the concentration of delta-3-carene and its oxidation products. This concentration has an effect on the reaction kinetics.

Mixing: Efficient mixing of reactants must be used. If the reaction is run without stirring, it takes a long time for the potassium

permanganate to react completely (over 50 hours). This is apparently due to potassium permanganate not dissolving in the acetone phase. Possibly the manganese dioxide formed during the reaction covers the potassium permanganate crystals and prevents them from contacting and dissolving in the solvent.

Periodic Removal of Oxidation Products: Since most of the oxidation products are adsorbed on the manganese dioxide surface, they may be removed from the system by manganese dioxide removal (filtration). One run was made to investigate the effect of intermittant oxidation product removal on product distribution. One-third of the total amount of potassium permanganate was added, reacted, and the manganese dioxide removed by filtration. This was repeated two more times. There was no significant change in the distribution of cis- and trans-caronic acid and cis-homocaronic acid. The main effect was to reduce the number and amount of minor oxidation products. This effect was not important enough for incorporation into the batch process for cis-caronic acid production (Section III-N).

Acetone Solvent

Acetone is a suitable solvent for the oxidation reaction. It dissolves potassium permanganate (1.8 g/100 ml at 16°C) and is miscible with delta-3-carene. Only 5% of the total amount of potassium permanganate in the system reacts with the acetone (Section III-L). Unreacted delta-3-carene remains in the acetone phase while most of the oxidation products are adsorbed on the manganese dioxide.

Recovery of Oxidation Products

Two methods of oxidation product recovery were explained in Section III-L. For small scale (less than ten grams of delta-3-carene oxidized) experiments where recovery of all of the oxidation product was desired, the reaction of manganese dioxide with sodium bisulfite to form manganous sulfate was used. The result was a water solution of all of the oxidation products that could be extracted with ether. The only oxidation products not recovered were those not recoverable in the ether extraction step.

In larger scale work (oxidation of over ten grams of delta-3-carene) as the batch process for the production of cis-caronic acid from delta-3-carene (Section III-N), most of the oxidation products were removed from the manganese dioxide by washing it with hot water. Assuming that one mol of manganese dioxide is produced per mol of potassium permanganate reacted, the theoretical production of manganese dioxide (Section III-L) was 120 g. The weight of the manganese dioxide plus oxidation products after water removal was 127 g. The total amount of oxidation products was 45 g. Therefore, at least 85 percent of the oxidation products were recovered from the manganese dioxide.

In retrospect, the recovery of the oxidation products from the manganese dioxide surface would perhaps have been more efficient if a five percent potassium hydroxide solution had been used instead of water, since the oxidation products are more soluble in basic than in neutral solutions.

D. Separation and Purification of Oxidation Products

The methods used for product separation and purification were explained in Section III-M. The basis of the separation is that the relative solubilities of the oxidation products in water vary depending on the pH of the solution. Thus the ether extraction of the water solution at various pH levels produces extracts that have different compositions. In general, as the pH is lowered, the oxidation products become less soluble in the water phase and easier to remove by ether extraction.

Manual Extraction Study

The process used (Section III-M) for separating cis-caronic acid from the mixture of oxidation products was based on the results of the manual extraction study. The following procedure was used on a water solution of the oxidation products:

1. The pH of the water solution was adjusted.
2. The solution was extracted four times manually with ether.
3. The water solution was adjusted to pH <1.
4. The solution was extracted again as in Step 2.

The pH of the water solution (Step 1) was varied. The water was removed from the extracts with anhydrous magnesium sulfate (Section III-E) and the ether evaporated. The results are shown in Table II.

On standing, crystals formed in the extracts from the pH <1 water solutions in Trials 1 and 2. The crystals were removed and identified as cis-caronic acid. The method of final crystal removal and purification is discussed in Section III-M.

Continuous Extraction Study

Another application of ether extraction of a water solution of oxidation products with pH control was also briefly investigated. The procedure was as follows:

1. Adjust the pH of the water solution of pH = 6.4.
2. Extract continuously with ether for 24 hours.
3. Readjust to pH = 5.0.
4. Repeat Step 2.
5. Readjust to pH = 4.0.
6. Continue the process for pH = 2.8, 1.4, 1.0.

The study was of general interest only, since it was more complicated than the process described in Section III-M and gave no better results.

Crystal Separation and Purification

The method reported in the literature for the removal of cis-caronic acid from a mixture of viscous liquid phase oxidation products was to boil the mixture with an equal volume of chloroform and filter (9). This method works well since pure, clean crystals are recovered, but about fifty percent of the crystals dissolve in the

boiling chloroform. A more efficient method involves mixing one volume of oxidation products with one volume of chloroform and filtering under vacuum (Section III-M).

E. Batch Process for the Production of Cis-Caronic Acid from Delta-3-Carene in 6.5% Yield

The batch process presented in Section III-N under the same heading, and summarized in Figure 18, is the most efficient method for cis-caronic acid production that resulted from this research. The process has not been optimized, but inefficiencies and unnecessary steps have been eliminated wherever possible.

Table II. Manual Extraction Study

Trial No.	Weight Oxid. Prod. in Sol'n, g.	Vol. of Sol'n, ml	First Extraction*		Second Extraction*		Total Wt. Extract, g.
			pH of Sol'n	Wt. Extract, g.	pH of Sol'n	Wt. Extract, g.	
1	2.92	50	3.2	1.19	<1	.70	1.89
2	3.02	50	3.9	.94	<1	.92	1.86
3	3.06	50	5.0	.47	<1	1.39	1.86

V CONCLUSIONS

1. Cis- and trans-caronic acids and cis-homocaronic acid were identified and found to be present in the oxidation products resulting from the potassium permanganate oxidation of delta-3-carene in acetone.

2. The method reported in the literature (7) for the separation and purification of trans-caronic acid via the ammonium salt (Section III-M) was confirmed.

3. A method (Sections III-M and IV-D) for the separation and purification of cis-caronic acid from the oxidation products resulting from the potassium permanganate oxidation of delta-3-carene in acetone was developed.

4. A mixture of cis-homocaronic acid and a hydroxy carboxylic acid was produced.

5. The oxidation product resulting from the dichromate oxidation of delta-3-carene contained essentially no cis- or trans-caronic acids. The solid material that precipitated out of the mixture of oxidation products was tentatively identified as a lactone, terebic acid.

VI RECOMMENDATIONS

Cis- and trans-caronic acids and cis-homocaronic acid have been identified as components of the oxidation product from the potassium permanganate oxidation of delta-3-carene in acetone. A process for the production of cis-caronic acid from delta-3-carene in 6.5% yield has been developed.

I recommend that the research on the production of cyclopropane ring-containing dibasic acids from delta-3-carene be continued in order to make one or more of the acids available to interested research organizations. This would help in the market development of delta-3-carene. The specific areas recommended for future research are listed below:

1. Optimize the existing process (Sections III-N and IV-E).
2. Separate the mixture of crystals (cis-homocaronic acid and the hydroxy carboxylic acid) recovered from the pH = 4.0 extract (Sections III-M and IV-D).
3. Develop a pilot plant scale process for the production of cis-caronic acid from delta-3-carene.
4. Investigate the use of different oxidizing systems such as:
    (a) hydrogen peroxide
    (b) air oxidation
    (c) potassium permanganate in acidic and basic water solutions.

VII APPENDIX

Cis-Caronic Acid

Trans-Caronic Acid

Cis-Homocaronic Acid

Trans-Homocaronic Acid

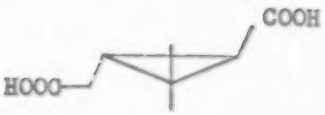
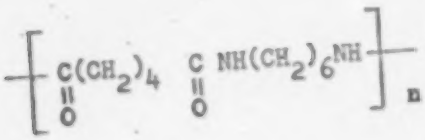
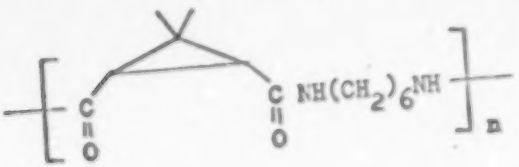


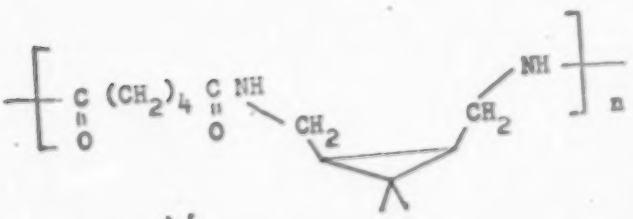
Figure 2. Cyclopropane Ring-Containing Dicarboxylic Acids Derived from Delta-3-Carene

A. Reference; Nylon 6.6 (DuPont)



B. Combinations Using Cis-Caronic Acid and Related Diamine





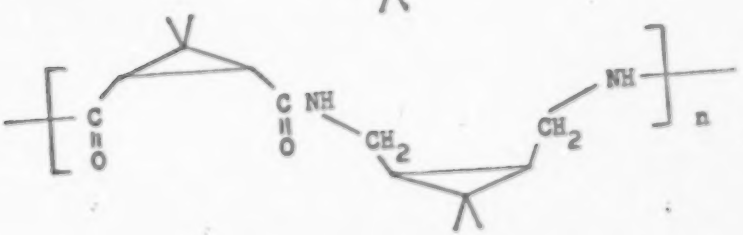
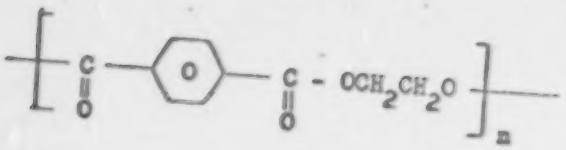


Figure 3. Potential Polyamides Using Cis-Caronic Acid

A. Reference; Dacron (Polyethylene Terephthalate)



B. Substitution of Dimethyl Cis-Caronate for Dimethyl Terephthalate (Polyethylene Cis-Caronate)

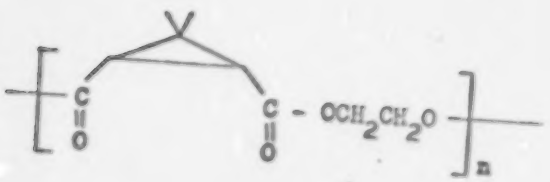


Figure 4. Potential Polyester Using Dimethyl Cis-Caronate

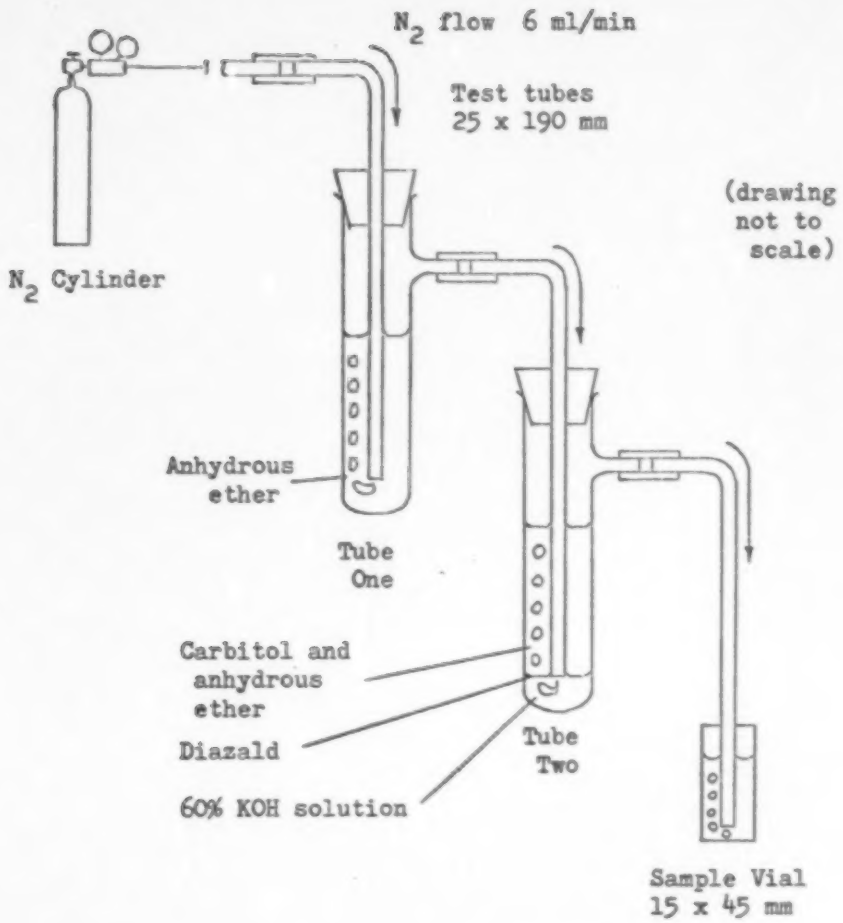


Figure 5. Apparatus for Esterification Using Diazomethane

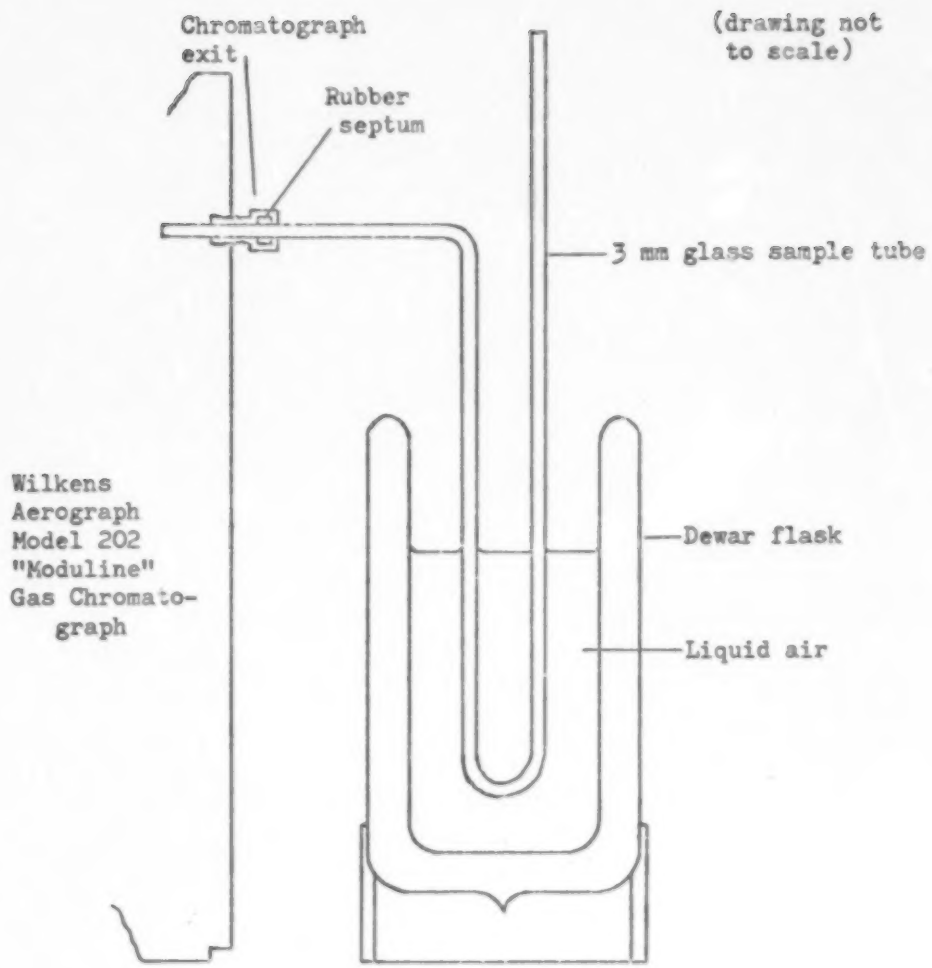


Figure 6. Sample Collection in Preparative Gas Chromatography

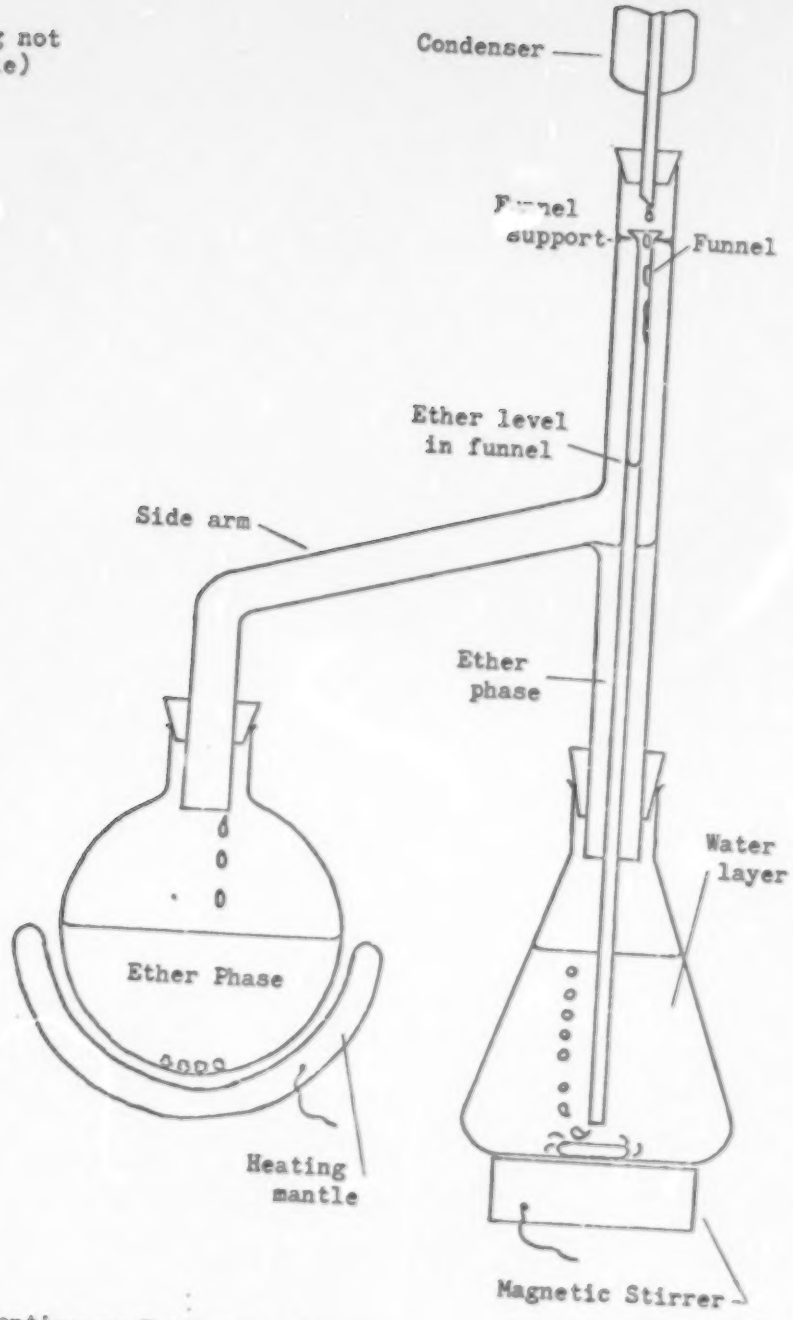


Figure 7. Continuous Extraction Apparatus

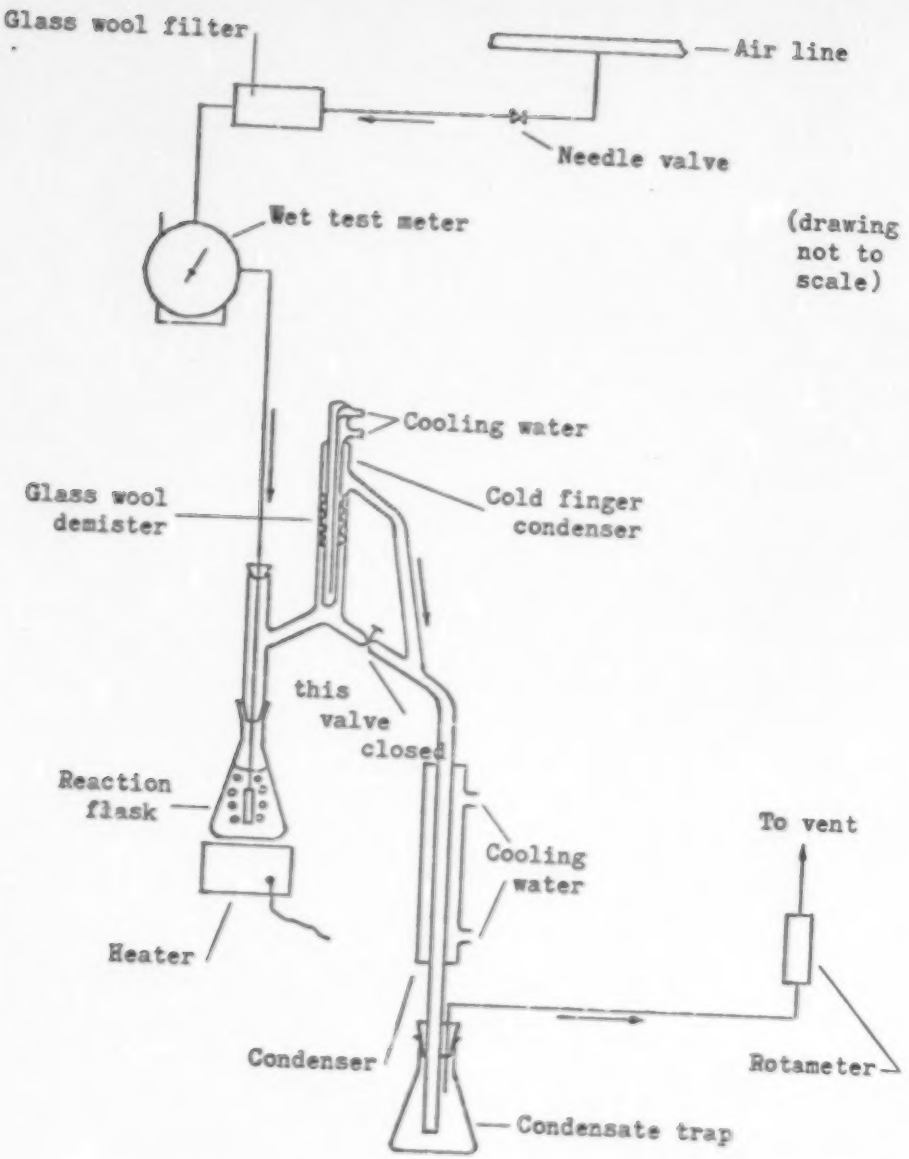


Figure 8. Reaction System for Catalytic Liquid-Phase Air Oxidation

(drawing not to scale)

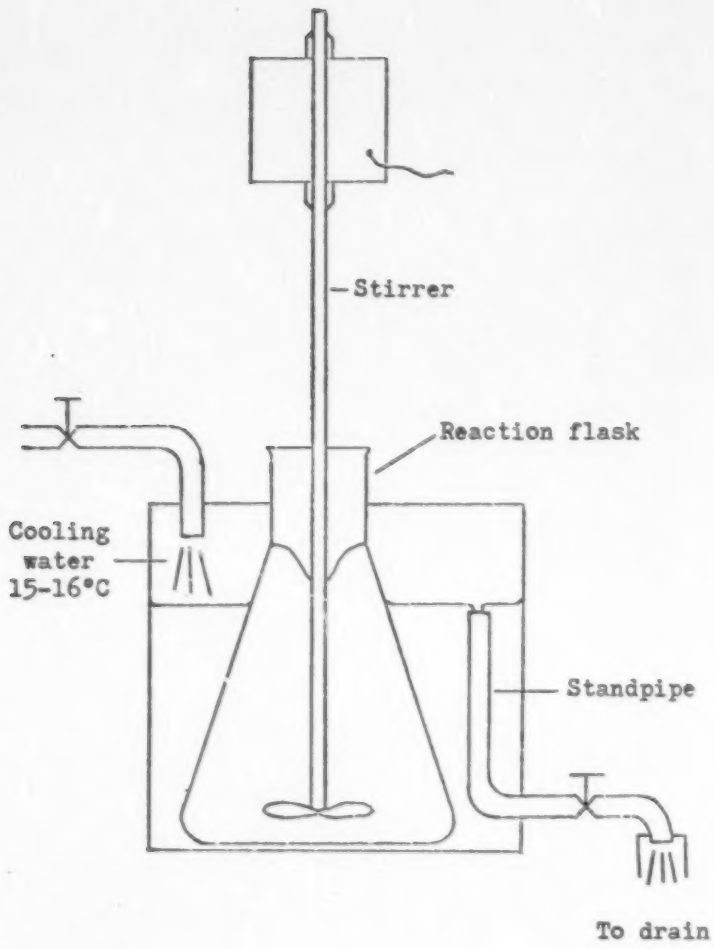
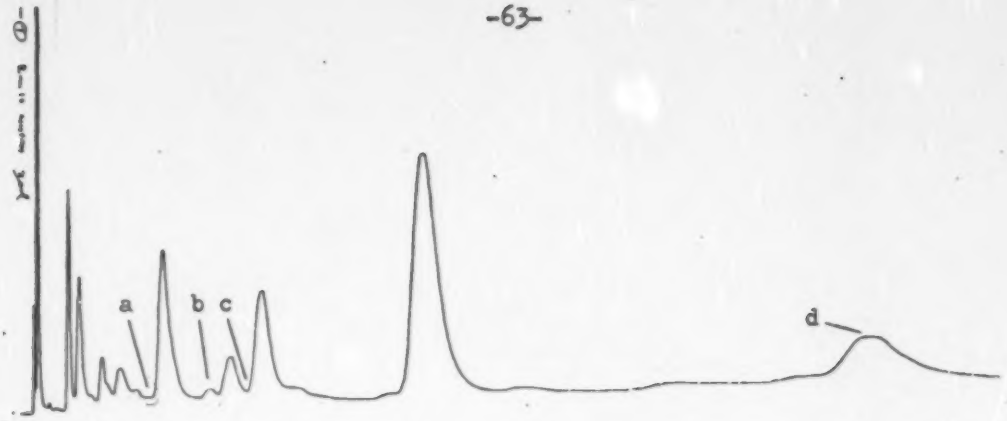


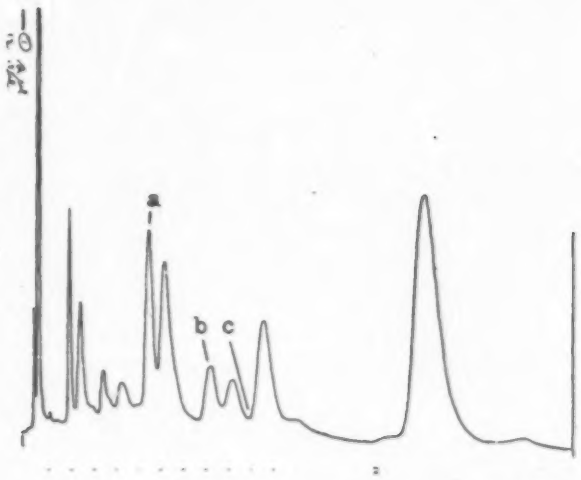
Figure 9. Apparatus for Potassium Permanganate Oxidation of Delta-3-Carene in Acetone



A. Methyl Ester of Oxidation Product

Peak Identification

a -- dimethyl trans-caronate
b -- dimethyl cis-caronate
c -- dimethyl cis-homocaronate
d -- methyl terebate



B. Methyl Ester of Oxidation Product Plus Dimethyl Trans-Caronate and Dimethyl Cis-Caronate

Figure 10. Gas Chromatogram of the Methyl Ester of the Oxidation Product Resulting from the Dichromate Oxidation of Delta-3-Carene

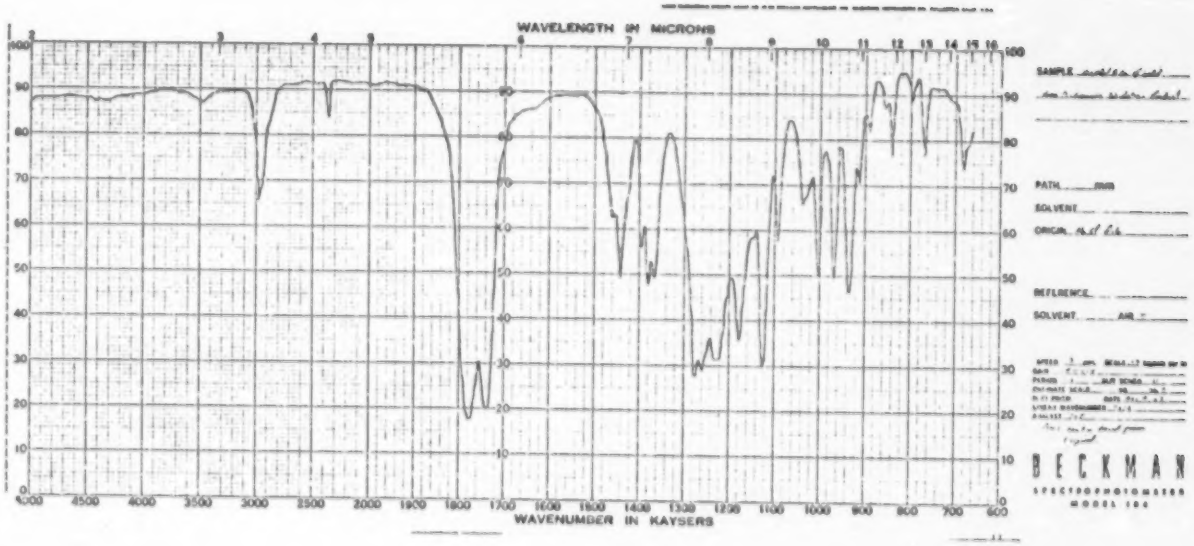


Figure 11. Infrared Spectrum of the Methyl Ester of the Crystalline Product Recovered from the Oxidation Products Resulting from the Dichromate Oxidation of Delta-3-Carene.
Tentative Identification: Methyl Terebate

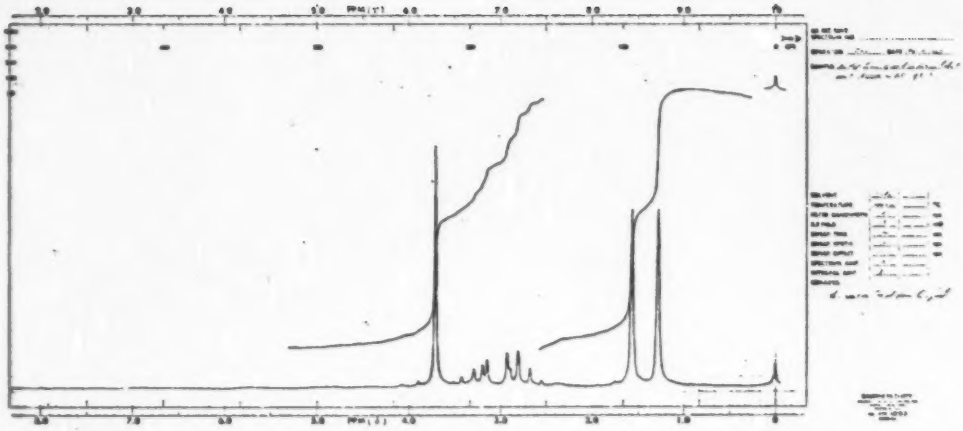
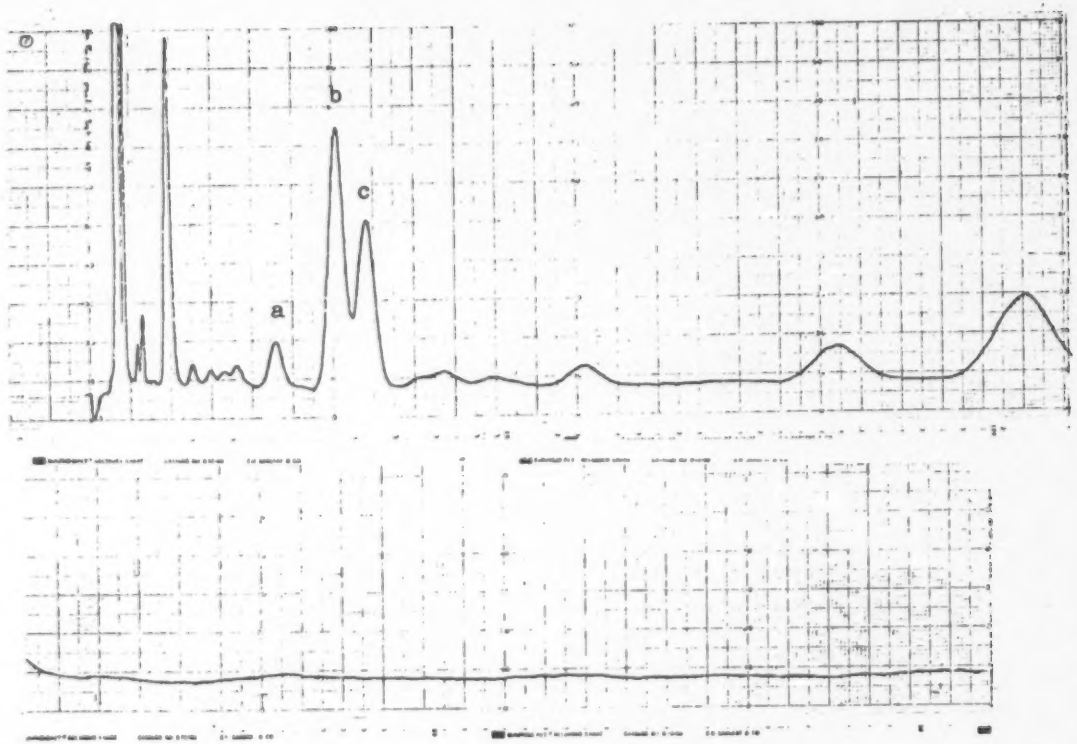
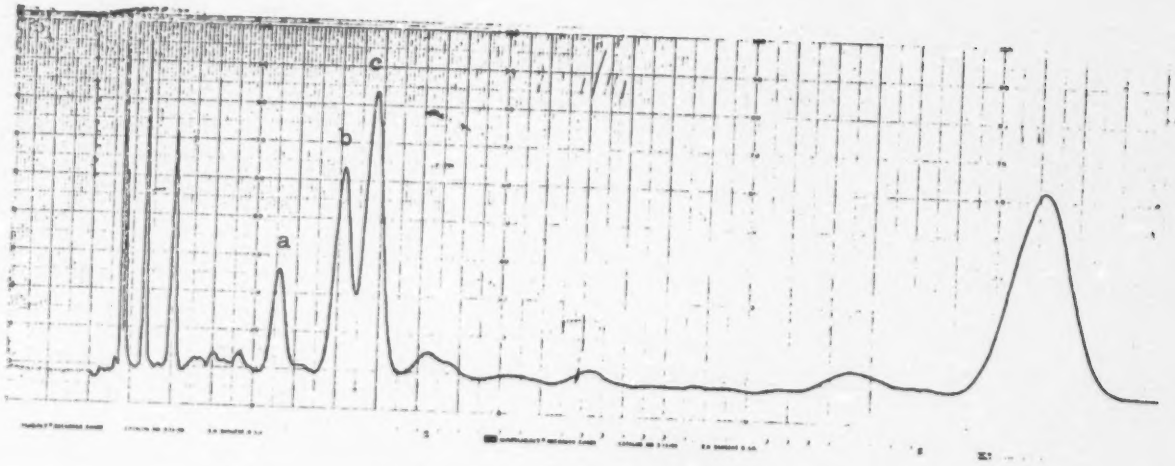


Figure 12. Nuclear Magnetic Resonance Spectrum of the Methyl Ester of the Crystalline Product Recovered from the Oxidation Products Resulting from the Dichromate Oxidation of Delta-3-Carene. Tentative Identification: Methyl Terebate



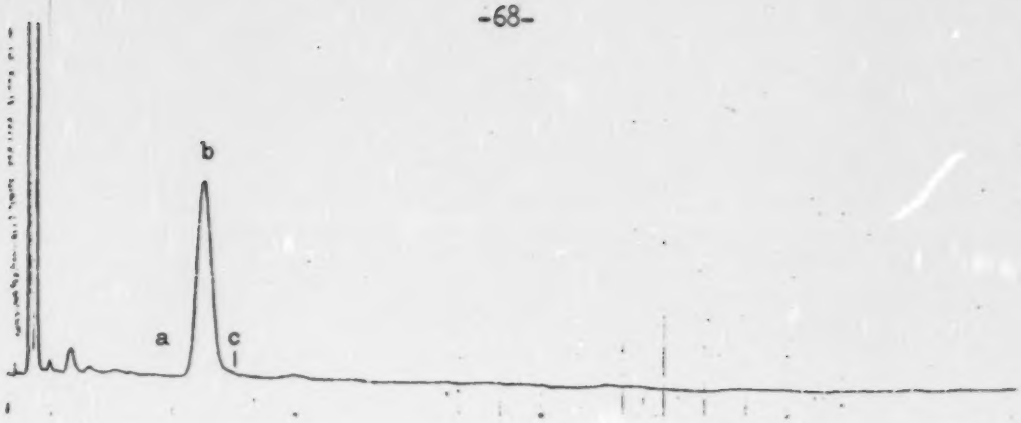
Peak Identification: a -- dimethyl trans-caronate
b -- dimethyl cis-caronate
c -- dimethyl cis-homocaronate

Figure 13. Gas Chromatogram of the Methyl Ester of the Oxidation Product Resulting from the Potassium Permanganate Oxidation of Delta-3-Carene in Acetone



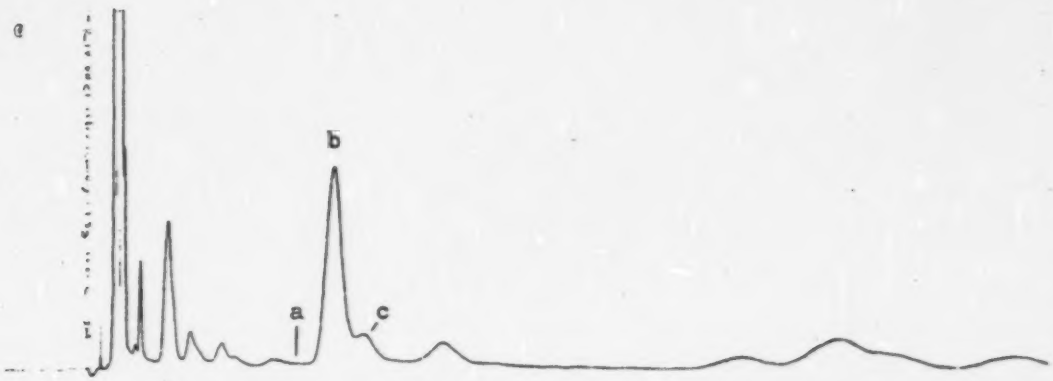
Peak Identification: a -- dimethyl trans-caronate
b -- dimethyl cis-caronate
c -- dimethyl cis-homocaronate

Figure 14. Gas Chromatogram of the Methyl Ester of the pH = 3.0 Extract of a Water Solution of the Oxidation Products Resulting from the Potassium Permanganate Oxidation of Delta-3-Carene in Acetone



A. Methyl Ester of the Extract Before Removal of Cis-Caronic Acid Crystals.

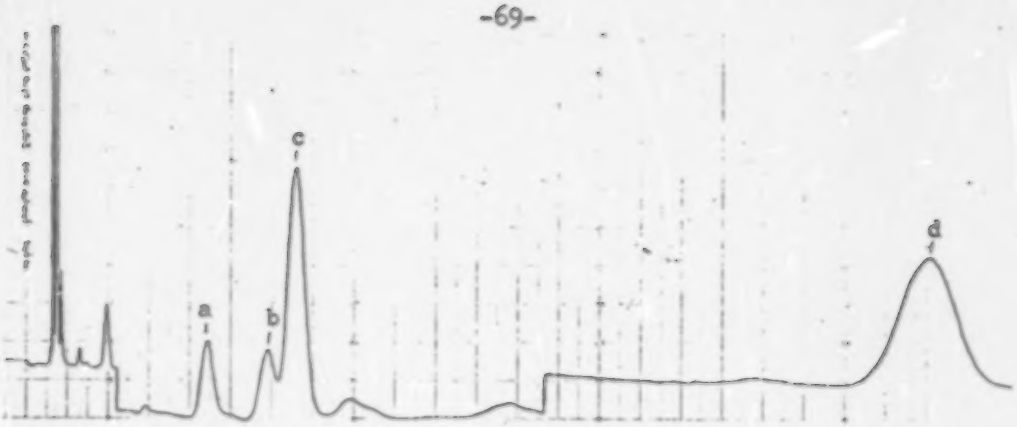
Peak Identification: a -- dimethyl trans-caronate
b -- dimethyl cis-caronate
c -- dimethyl cis-homocaronate



B. Methyl Ester of the Extract After Removal of the Cis-Caronic Acid Crystals

Figure 15. Gas Chromatogram of the Methyl Ester of the pH <1 Extract of a Water Solution of the Oxidation Products* Previously Extracted at pH = 3.0

* From $KMnO_4$ Oxidation of Delta-3-Carene in Acetone



A. Methyl Ester of the Extract Before Removal of Crystals

Peak Identification:
a -- dimethyl trans-caronate
b -- dimethyl cis-caronate
c -- dimethyl cis-homocaronate
d -- a methyl hydroxy-carboxylate

B. Methyl Ester of the Extract After Removal of the Crystals

Figure 16. Gas Chromatogram of the Methyl Ester of the pH = 4.0 Extract of a Water Solution of the pH = 3.0 Extract*.

* The pH = 3.0 Extract referred to in Figure 14.

C. Methyl Ester of Crystal.

See Figure 20 for Infrared Spectrum of Pure c (First Compound)

See Figure 22 for Infrared Spectrum of Pure d (Second Compound)

See Figure 26 for Nuclear Magnetic Resonance Spectrum of Pure c and Pure d.

Figure 16 continued.

A. Methyl Ester of Extract Before Removal of Cis-Caronic Acid Crystals

Peak Identification: a -- dimethyl trans-caronate
b -- dimethyl cis-caronate
c -- dimethyl cis-homocaronate

B. Methyl Ester of Extract After Removal of Cis-Caronic Acid Crystals

Figure 17. Gas Chromatogram of the Methyl Ester of the pH (1 Extract of a Water Solution of the pH = 3.0 Extract* Previously Extracted at pH = 4.0

* The pH = 3.0 Extract referred to in Figure 14.

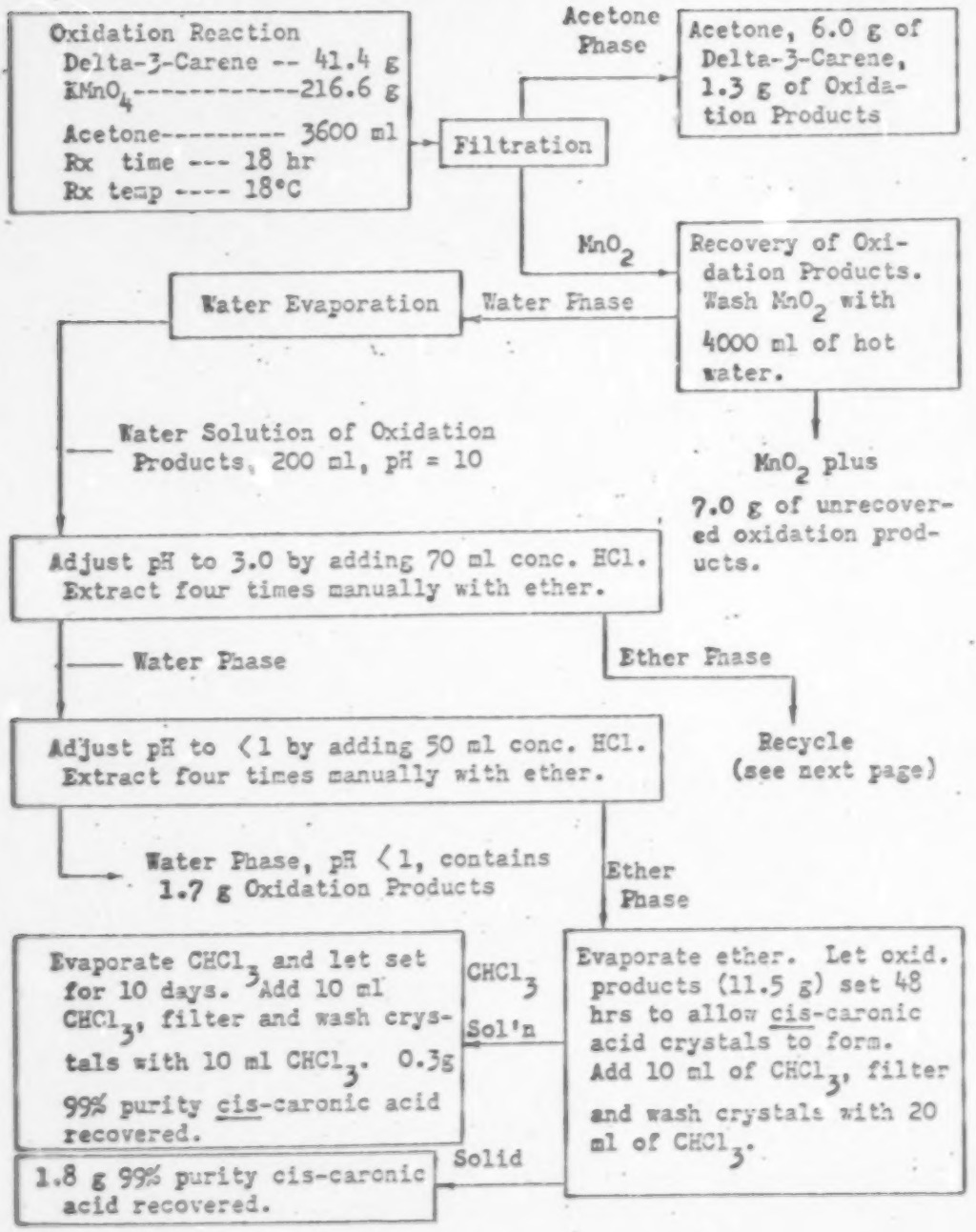

Oxidation Reaction
Delta-3-Carene -- 41.4 g
KMnO4----------216.6 g
Acetone--------- 3600 ml
Rx time --- 18 hr
Rx temp ---- 18°C
Acetone Phase
Acetone, 6.0 g of Delta-3-Carene, 1.3 g of Oxidation Products
Filtration
MnO2
Recovery of Oxidation Products. Wash MnO2 with 4000 ml of hot water.
Water Evaporation
Water Phase
Water Solution of Oxidation Products, 200 ml, pH = 10
MnO2 plus 7.0 g of unrecovered oxidation products.
Adjust pH to 3.0 by adding 70 ml conc. HCl. Extract four times manually with ether.
Water Phase
Ether Phase
Adjust pH to <1 by adding 50 ml conc. HCl. Extract four times manually with ether.
Recycle (see next page)
Water Phase, pH <1, contains 1.7 g Oxidation Products
Ether Phase
Evaporate CHCl3 and let set for 10 days. Add 10 ml CHCl3, filter and wash crystals with 10 ml CHCl3. 0.3g 99% purity cis-caronic acid recovered.
CHCl3 Sol'n
Evaporate ether. Let oxid. products (11.5 g) set 48 hrs to allow cis-caronic acid crystals to form. Add 10 ml of CHCl3, filter and wash crystals with 20 ml of CHCl3.
Solid
1.8 g 99% purity cis-caronic acid recovered.

Figure 18. Batch Process for the Production of Cis-Caronic Acid from Delta-3-Carene in 6.5% Yield.

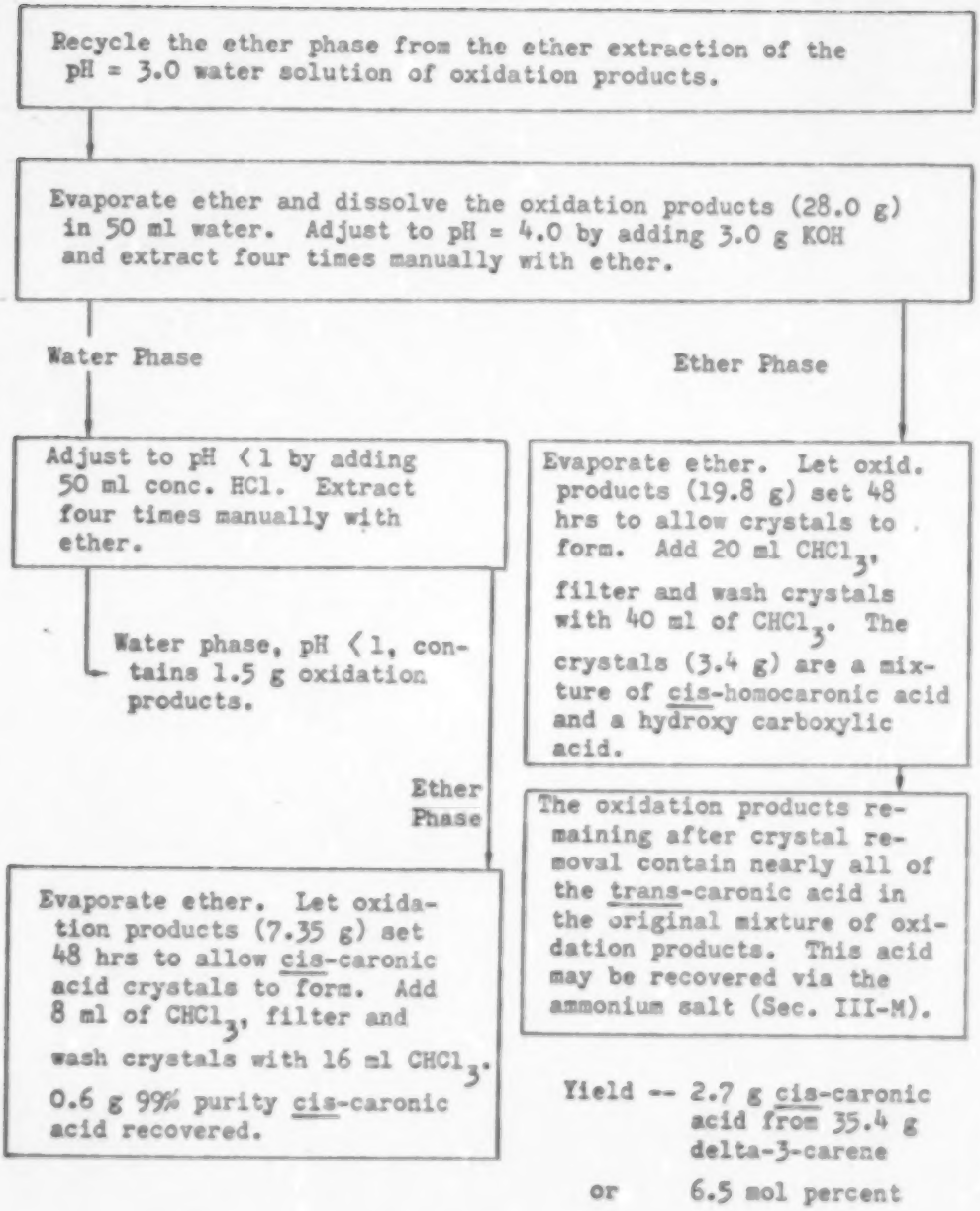

Recycle the ether phase from the ether extraction of the pH = 3.0 water solution of oxidation products.
Evaporate ether and dissolve the oxidation products (28.0 g) in 50 ml water. Adjust to pH = 4.0 by adding 3.0 g KOH and extract four times manually with ether.
Water Phase
Ether Phase
Adjust to pH < 1 by adding 50 ml conc. HCl. Extract four times manually with ether.
Water phase, pH < 1, contains 1.5 g oxidation products.
Ether Phase
Evaporate ether. Let oxidation products (7.35 g) set 48 hrs to allow cis-caronic acid crystals to form. Add 8 ml of CHCl3, filter and wash crystals with 16 ml CHCl3. 0.6 g 99% purity cis-caronic acid recovered.
Evaporate ether. Let oxid. products (19.8 g) set 48 hrs to allow crystals to form. Add 20 ml CHCl3, filter and wash crystals with 40 ml of CHCl3. The crystals (3.4 g) are a mixture of cis-homocaronic acid and a hydroxy carboxylic acid.
The oxidation products remaining after crystal removal contain nearly all of the trans-caronic acid in the original mixture of oxidation products. This acid may be recovered via the ammonium salt (Sec. III-M).
Yield -- 2.7 g cis-caronic acid from 35.4 g delta-3-carene
or 6.5 mol percent

Figure 18 continued.

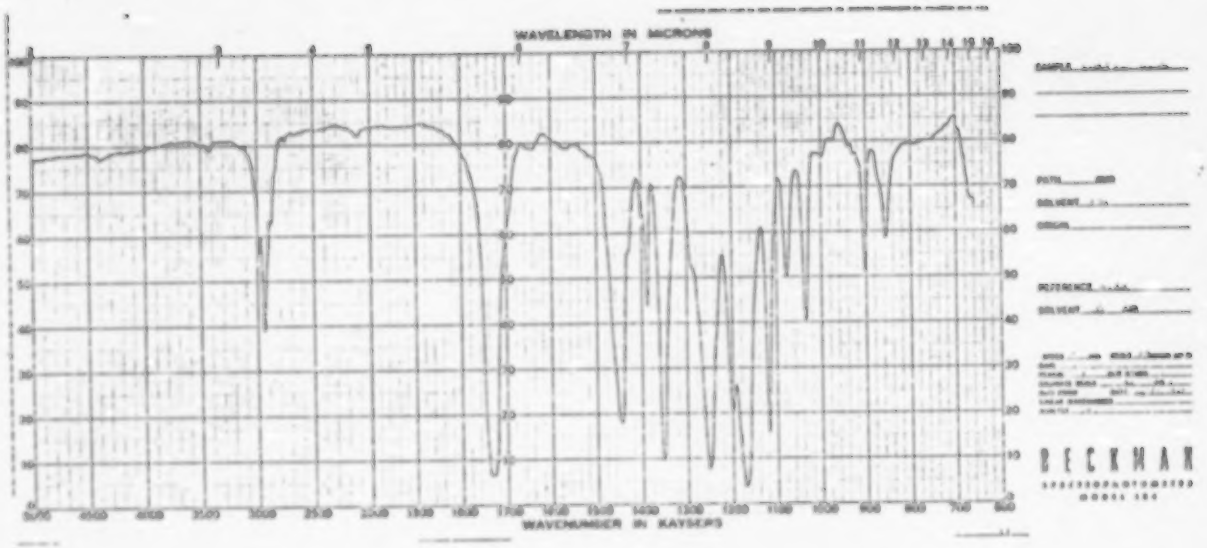


Figure 19. Infrared Spectrum of Dimethyl Trans-Caronate from the Trans-Caronic Acid Separated from the Oxidation Products Resulting from the Potassium Permanganate Oxidation of Delta-3-Carene in Acetone.

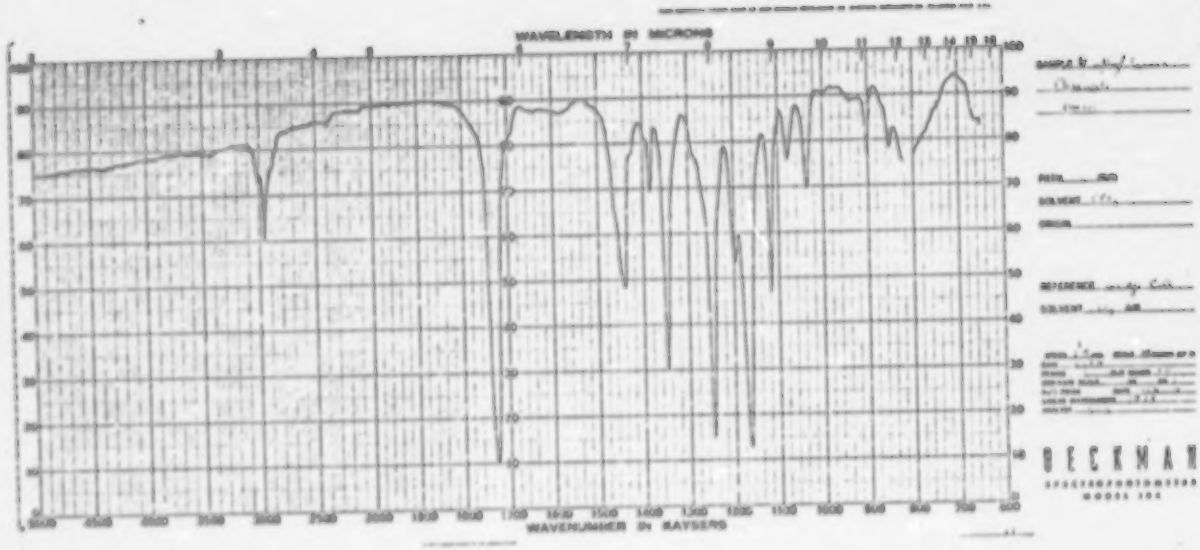


Figure 20. Infrared Spectrum of Dimethyl Trans-Caronate from the Trans-Caronic Acid Sample Obtained from Dr. Masanao Matsui, University of Tokyo, Tokyo, Japan.

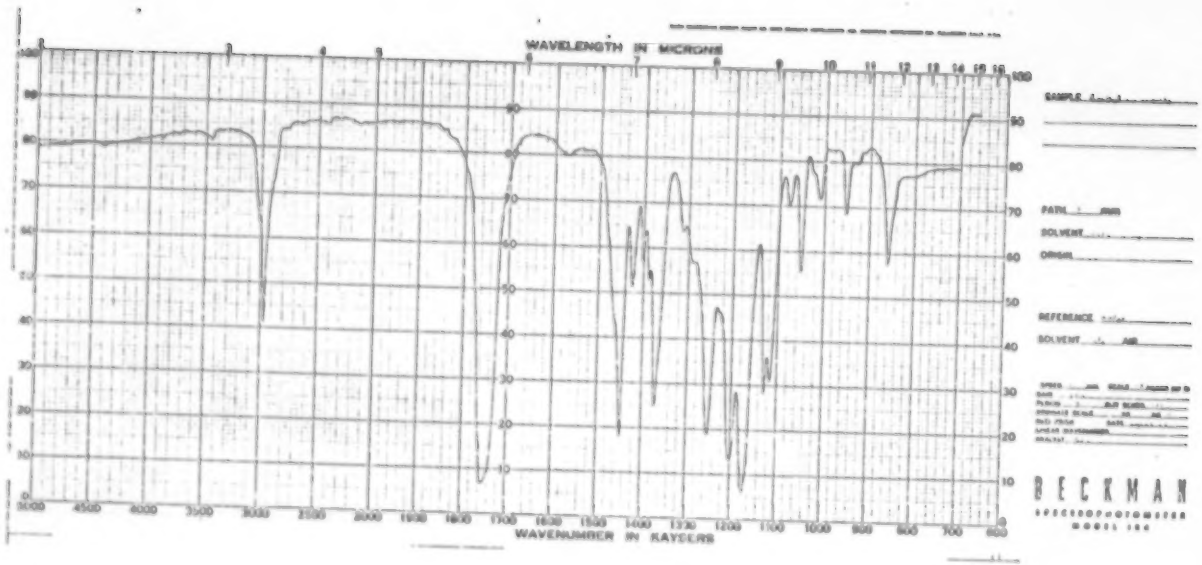


Figure 21. Infrared Spectrum of Dimethyl Cis-Caronate from the Cis-Caronic Acid Separated from the Oxidation Products Resulting from the Potassium Permanganate Oxidation of Delta-3-Carene in Acetone.

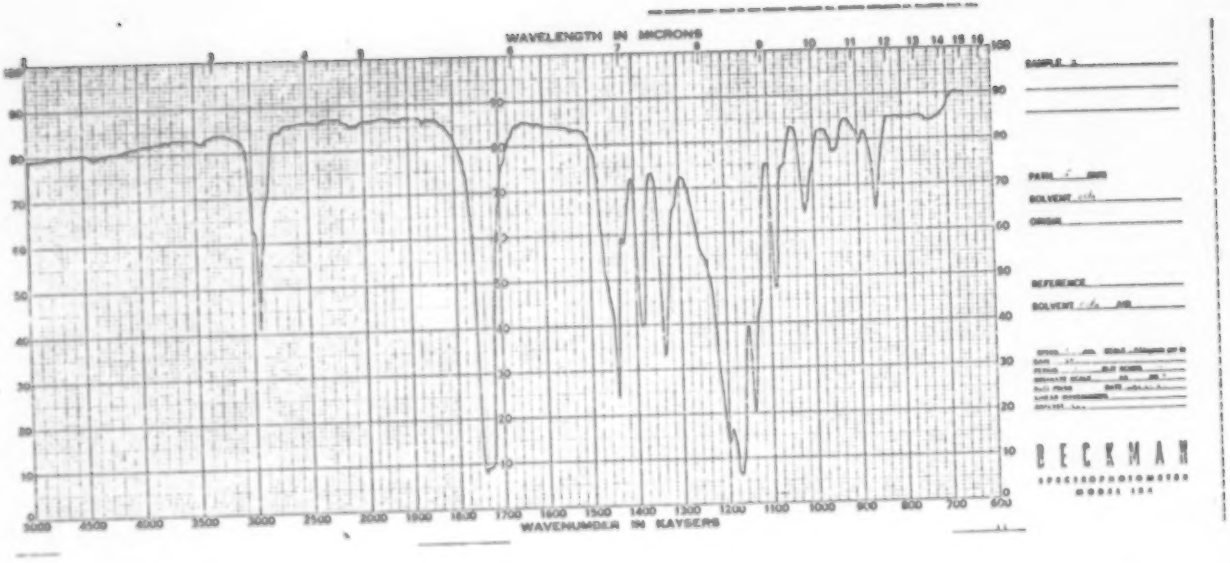


Figure 22. Infrared Spectrum of the Methyl Ester of the First (see Figure 16) of the Two Compounds in the Crystalline Material Separated from the pH = 4.0 Extract (see Figure 16) Formed as Part of the Separation of the Oxidation Products Resulting from the Potassium Permanganate Oxidation of Delta-3-Carene in Acetone. The ester has been identified as dimethyl cis-homocaronate.

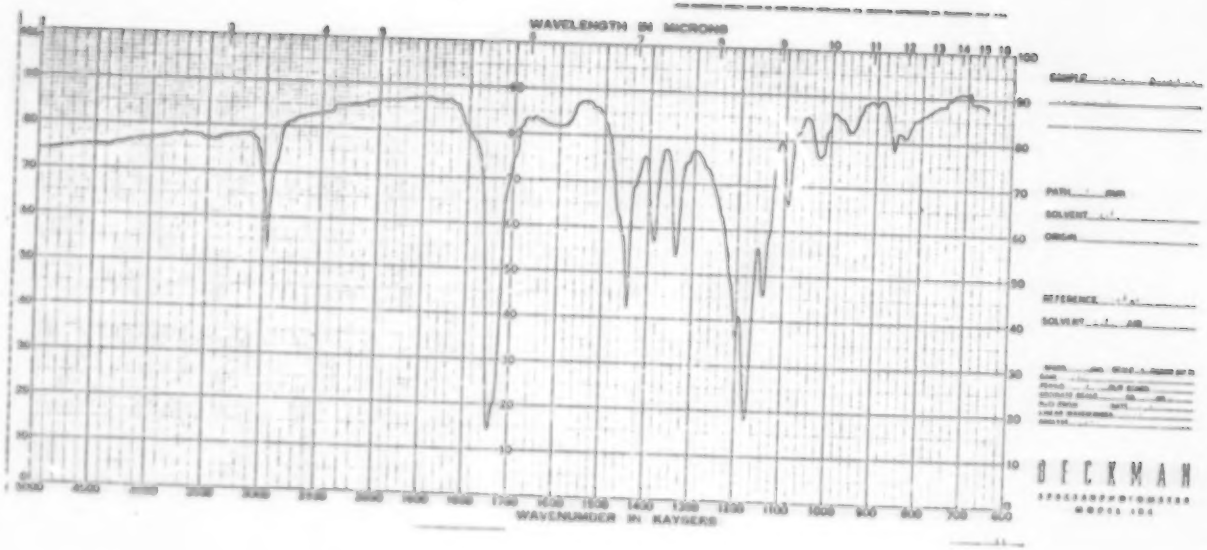


Figure 23. Infrared Spectrum of Dimethyl Cis-Homocaronate from the Cis-Homocaronic Acid Sample Obtained from Dr. Masanao Matsui, University of Tokyo, Tokyo, Japan.

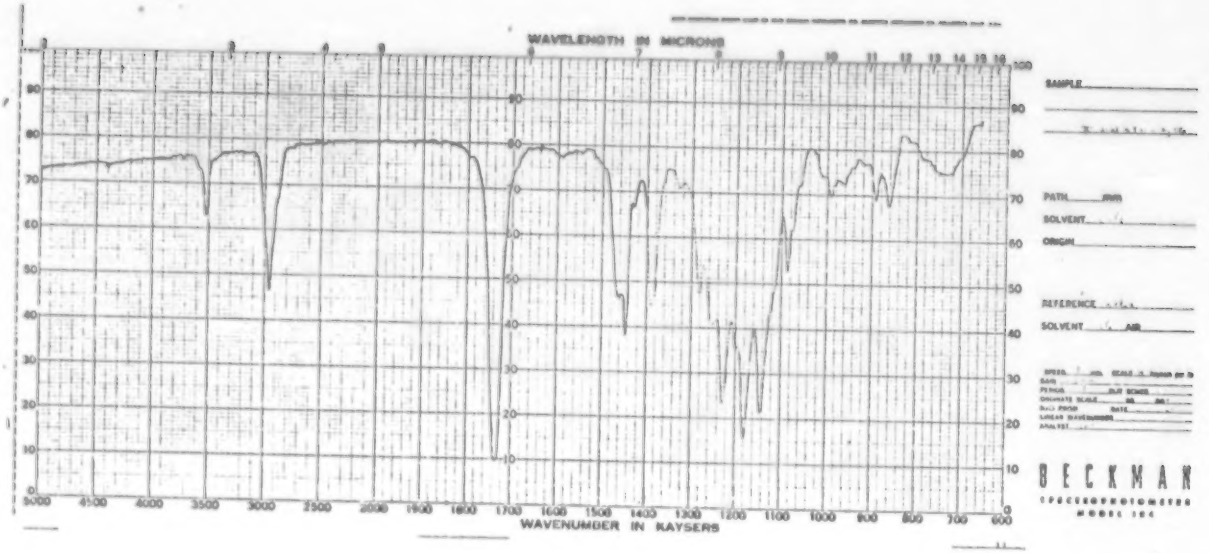


Figure 24. Infrared Spectrum of the Methyl Ester of the Second (see Figure 16) of the Two Compounds in the Crystalline Material Separated from the pH = 4.0 Extract (see Figure 16) Formed as Part of the Separation of the Oxidation Products Resulting from the Potassium Permanganate Oxidation of Delta-3-Carene in Acetone.

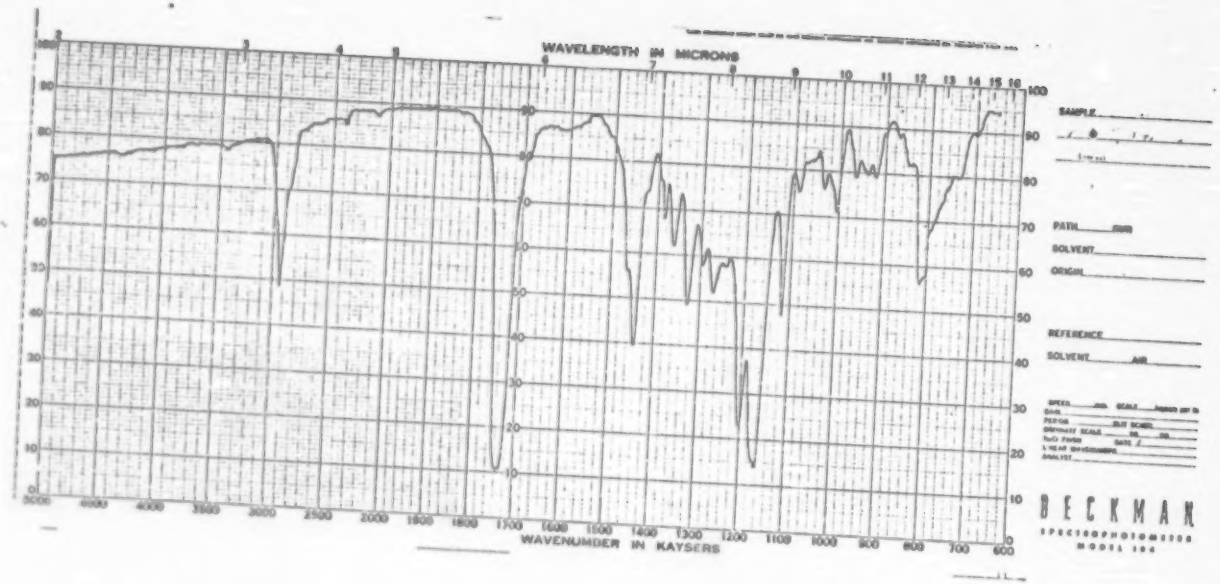


Figure 25. Infrared Spectrum of Dimethyl Trans-Homocaronate from the Trans-Homocaronic Acid Sample Obtained from Dr. Masanao Matsui, University of Tokyo, Tokyo, Japan.

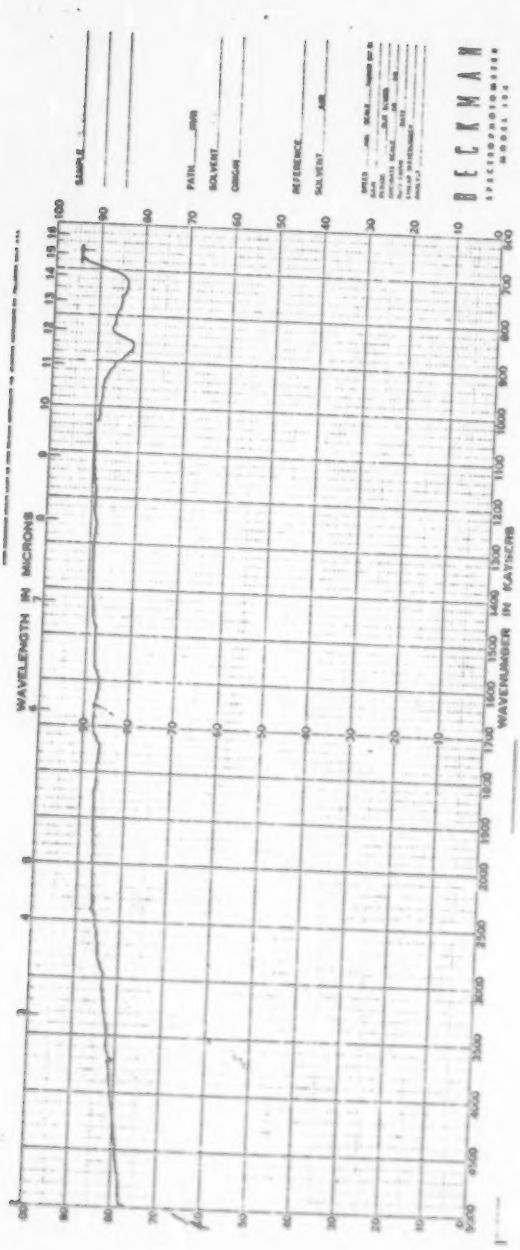


Figure 26. Infrared Spectrum of Carbon Tetrachloride Blanked Out by Carbon Tetrachloride in Reference Beam.

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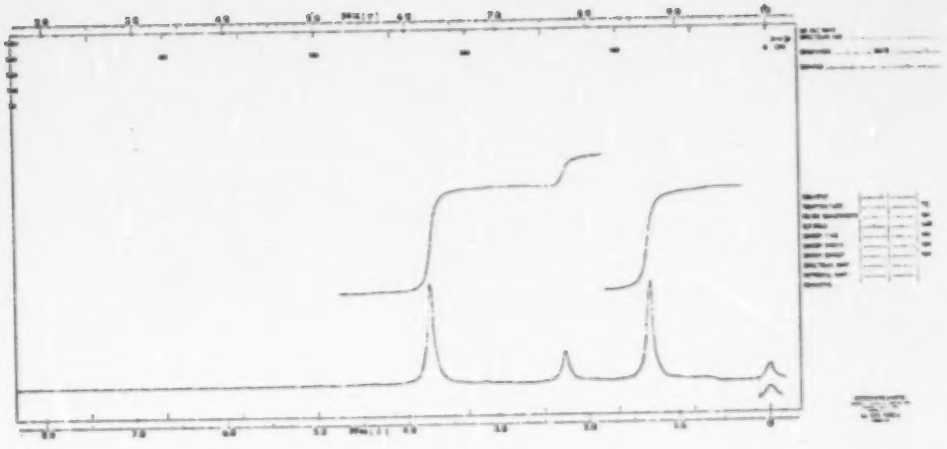
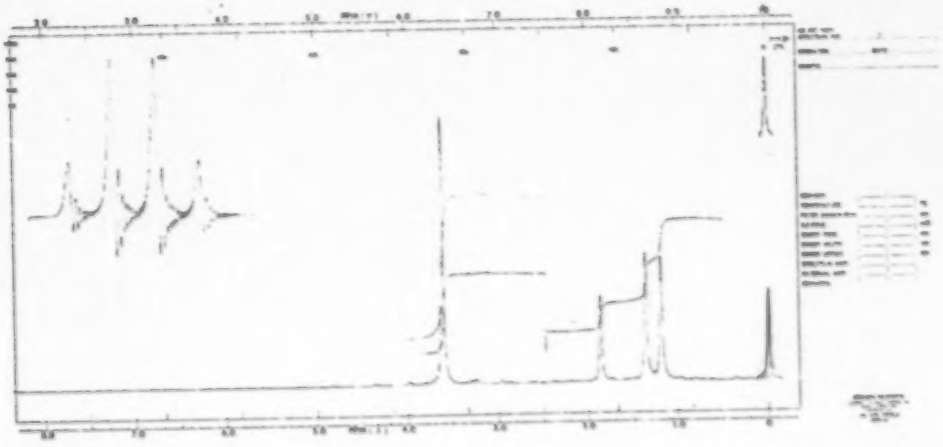
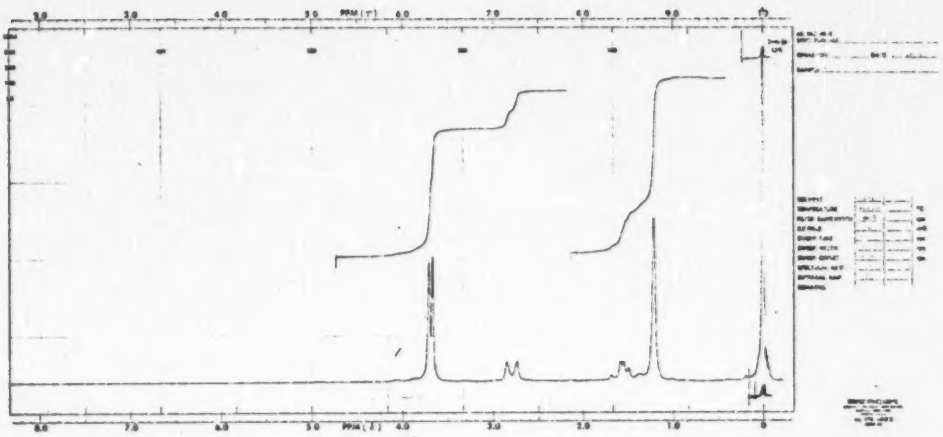


A. NMR Spectrum of Dimethyl Trans-Caronate

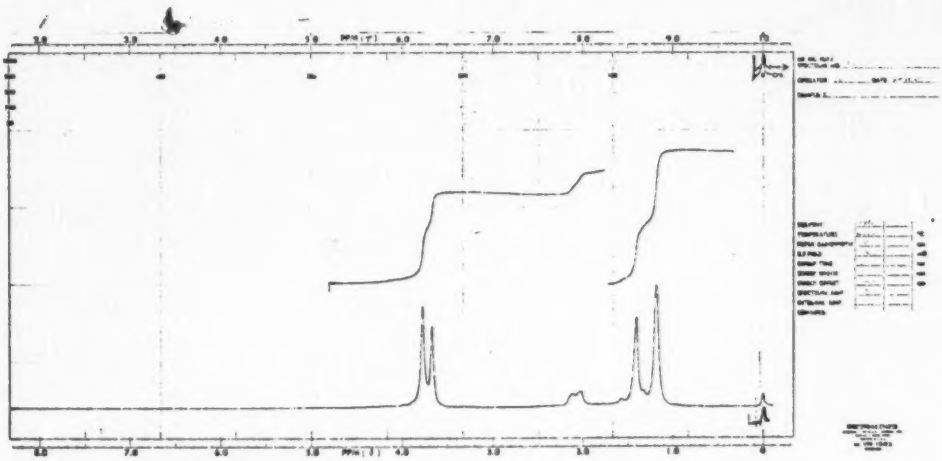


B. NMR Spectrum of Dimethyl Cis-Caronate

Figure 27. Nuclear Magnetic Resonance Spectra of the Dimethyl Caronates from the Caronic Acids Separated from the Mixture of Oxidation Products Resulting from the Potassium Permanganate Oxidation of Delta-3-Carene in Acetone.



A. NMR Spectrum of the First Compound (see Figure 16)



B. NMR Spectrum of the Second Compound (see Figure 16)

Figure 28. Nuclear Magnetic Resonance Spectra of the Methyl Esters of the Two Compounds that were in the Crystalline Material Recovered from the pH = 4.0 Extract (see Figure 16) Formed as Part of the Separation of the Mixture of Oxidation Products Resulting from the Potassium Permanganate Oxidation of Delta-3-Carene in Acetone.

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